



Analytical Electrochemistry: Beyond the Traditional Boundaries

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Abstract

This thesis presents five analytical electrochemistry projects which are written as separate chapters. The research presented herein covers a wide aspect of electrochemistry, ranging, experimentally, from a 'forensic-style' electrochemical analysis of the mercury/water biphasic system post-sonication, to studying the interaction of marine phytoplankton using electrochemistry, and theoretically, simulations providing new insights to non-ideal interactions in voltammetry leading to phase-transition like behaviour. The scientific scope of the chapters is broad and multi-disciplinary, some may even seem 'wacky'; but, they are all at-heart fundamentally based in electrochemistry and are adventurous projects pushing beyond the traditional boundaries of the current field. The novelty and scientific advances of each Chapter are summarised below.

Chapter 1 serves to introduce the fundamental concepts of electrochemistry, which are the building blocks for the projects discussed subsequently in this thesis. Here the discussion includes equilibrium electrochemistry, electrode kinetics and mass transport. Moreover, different aspect of electrochemistry in practice are discussed, such as the use of a three-electrode system, the effects of electrode geometry, and the voltammetric techniques – chronoamperometry and cyclic voltammetry.

For electrons to transfer across an electrode interface, the analyte must come within an electron tunnelling distance of the electrode. What if the analyte is insoluble in solution and the unavoidable sedimentation of solids voids contact with the electrode? Chapter 2 tackles this problem by facilitating the electrochemistry of insoluble solids with a bespoke carbon-black composite. The latter is used as a modification to the electrode so

as to bind the insoluble analyte, provide electrical contact and at the same time it is sufficiently porous allowing the composite to 'see' the electrolyte solution. The electrochemical behaviour of this composite material is fully characterised with three well-known aqueous insoluble redox couples, and are used to obtain the first cyclic voltammogram of solid red-cinnabar (α -HgS). Further highlighted in this Chapter is an in situ electrochemical X-ray diffraction experiment, facilitated by this carbon-black composite, demonstrating the possibility to electrochemically navigate across the narrow phase-width of the superconductor β -Fe_{1+x}Se post-synthesis.

What happens when ultra-sound sonication is applied to a mercury/water biphasic system? Chapter 3 presents a 'forensic-style' investigation, where the 'clouds' of grey particles seen emanating from the mercury/water interface were investigated and identified as Hg@HgO core-shell particles, characterised for the first time using a combination of electrochemical methods and X-ray diffraction experiments. Furthermore, as discovered electrochemically, sonication results in the simultaneous formation of molecular Hg(OH)₂ in the aqueous phase at a concentration close to a saturation limit of 0.24 mM; which is likely formed from the sonochemical reaction of liquid mercury with hydroxyl radicals; the latter is generated from acoustic cavitation.

Chapter 4 investigates the electrochemical interactions possible with marine phytoplankton. These are photosynthetic, chlorophyll-containing, single-cellular organisms which are globally significant as the nutritional source of all life forms in the ocean and has a dominant role in the ocean's carbon cycle. This Chapter showcases a pioneering in situ fluoro-electrochemical set up to quantify the rate of phytoplankton 'killed' by electro-oxidation. The electrochemical oxidation occurs via the propagation of hydroxyl radicals, formed at the electrode interface, reacting with the individual

phytoplankton distant from the electrode. Moreover, a total of six species of phytoplankton are screened to develop a proof-of-concept 'susceptibility library mapping' of phytoplankton species towards electro-oxidation.

Beyond the experimental-dominant work discussed thus far, theoretical simulations with a ground-up approach can often provide new insights from an entirely different perspective, which can synergistically augment or provoke experimental findings. In Chapter 5, the mathematical formulation, and numerical methods allowing electrochemical simulations are discussed. This Chapter builds upon the fundamental electrochemistry concepts as established in Chapter 1, enabling one to have full control over the simulation model – a contrast to a 'blackbox' approach.

Chapter 6 develops a general simulation model for voltammetry of species adsorbed from solution, involving coupled mass transport and adsorption which distinguishes the relative contributions from the adsorption kinetics, the mass transport and electron transfer kinetics of the reactants and products. The model adopts Langmuirian adsorption kinetics to allow the effects of adsorption on voltammetry to be generally accounted for. The new insights include: a steady-state voltage-current response for a macro-electrode when the rate-determining step becomes 'bottlenecked' by the slow desorption of the product. Furthermore, when the rate of adsorption and desorption of the reaction and product are fast compared to the mass transport and are not rate-determining, the simulated current for the redox process via the adsorption pathway can be up to several times higher to that when electron transfer occurs via the solution phase.

Continuing from the general adsorption model discussed in Chapter 6, Chapter 7 turns to investigate the effects of non-ideal surface interactions on voltammetry involving one

adsorbed species. In particular, the simulation focuses on non-ideal interactions leading to phase transition like behaviour, which is not uncommon in voltammetry reflecting strong surface interactions. By coupling interfacial electrode kinetics with the Frumkin adsorption isotherm, the underlining physicochemical processes occurring in voltammetry induced phase transitions are studied via simulation. Phase-transition-like behaviour is only observable in voltammetry under reversible electrode kinetics, which if not present would otherwise lead to a 'disconnection' from the adsorption isotherm. In the case when the phase transition occurs on the voltammetric timescale, the simulated interfacial conditions reveal intrusions into a 'forbidden' zone of the Frumkin adsorption isotherm – even in the presence of a significant excess in the concentration of the analyte – as a result of local dis-equilibrium.

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Glossary

Roman Symbols

Symbol	Meaning	Usual Units
a_i^α	activity of species i in phase α	mol m^{-3}
A	geometric area of the electrode	m^2
c^0	standard (unity) concentration	1 mol m^{-3}
$c_{i,0}$	surface concentration of species i	mol m^{-3}
$c_{i,bulk}$	bulk concentration of species i	mol m^{-3}
C	capacitance	F m^{-2}
D_i	diffusion coefficient of species i	$\text{m}^2 \text{ s}^{-1}$
E	applied potential	V
E^0	standard potential	V
E_f^0	formal potential	V
$E_{initial}$	initial applied potential	V
E_{switch}	reverse sweep potential	V
ΔE_{pp}	peak-to-peak separation	V
F	Faraday constant	$(96485.3) \text{ s A / mol}$
g	adsorbate-adsorbate interaction parameter	None
$g^\ddagger$	activated complex (transition state) – adsorbate interaction parameter	None
ΔG_θ°	Gibb's energy of adsorption	J
I	current	A
I_{cap}	capacitive current	A
I_{ss}	steady-state current	A
j	flux	$\text{mol cm}^{-2} \text{ s}^{-1}$
k_0	standard electrochemical rate constant	m s^{-1}

Symbol	Meaning	Usual Units
k'_0	standard electro-sorption rate constant	$\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$
k_{red}	reduction rate constant	m s^{-1}
k'_{red}	electro-adsorption rate constants	$\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$
k''_{red}	pre-exponential constant for electro-adsorption rate constant	$\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$
k_{ox}	oxidation rate constant	m s^{-1}
k'_{ox}	electro-desorption rate constants	s^{-1}
k''_{ox}	pre-exponential constant for electro-desorption rate constant	s^{-1}
m_T	mass transport coefficient	m s^{-1}
n	number of electrons transferred per reaction	none
n'	number of electrons transferred before the rate-determining step	none
p	pressure	N m^{-2}
r_e	radius of the electrode	m
R	ideal gas constant	$(8.314) \text{ J mol}^{-1} \text{ K}^{-1}$
R_s	resistance of the solution	Ω
R_u	uncompensated resistance	Ω
t	time	s
$t_{pot.on}$	time after potential step	s
t_{switch}	time of sweep reversal	s
T	temperature	K or $^{\circ}\text{C}$
T_c	critical temperature	K or $^{\circ}\text{C}$

Greek and Cyrillic Symbols

Symbol	Meaning	Usual Units
α	transfer coefficient	none
β	transfer coefficient	none
γ_i	activity coefficient of species i	none
Γ	truncation error	depends
Γ_i	surface coverage of species i	mol m ⁻²
δ	Nernst diffusion layer thickness	m
ε	tolerance level	none
η	over-potential ($E - E_f^0$)	V
θ	angle	°
λ	a) Numerical stability factor b) Wavelength	a) none b) m
Λ	reversibility parameter	none
μ_i^α	chemical potential for species i in phase α	J mol ⁻¹
$\mu_i^{0\alpha}$	standard chemical potential for species i in phase α	J mol ⁻¹
$\bar{\mu}_i^\alpha$	electrochemical potential for species i in phase α	J mol ⁻¹
ν	voltage scan rate	V s ⁻¹
ϕ^α	potential of phase α	V

Abbreviations

Abbreviation	Meaning
AQ	9,10-anthraquinone
AQH ₂	9,10-anthrahydroquinone
BPPG	basal plane pyrolytic graphite electrode
BSE	backscattering electron detector
CCAP	Culture Collection of Algae and Protozoa
CPE	carbon paste electrode
CV	cyclic voltammogram
FEG-SEM	field emission gun scanning electron microscopy
FWHM	full width half maximum
GC	glassy carbon
HER	hydrogen evolution reactions
IUPAC	International Union of Pure and Applied Chemistry
MSE	saturated mercury sulphate reference electrode
NA	numerical aperture
NHE	normal hydrogen electrode
NMP	N-methyl-2-pyrrolidone
OBD	oil blue N dye
ppm	part per million
PVDF	polyvinylidene fluoride
RCC	Roscoff Culture Collection
SCE	saturated calomel electrode
SDS	sodium dodecyl sulfate
SE	secondary electron detectors
SEM	scanning electron microscopy
UPD	under-potential deposition
UV	ultraviolet
XRD	X-ray diffraction

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Chapter 1 Introduction to Electrochemistry

What is electrochemistry? In my opinion, the quote from Alexander N. Frumkin, more of whom in Chapter 7, provided a definition which captures the essence:

*“Electrochemistry is a part of Chemical Physics, but a very singular part concerning the methods of investigation, character of regularities, and close connection with industry. Electrochemistry includes all the ways of interaction of moving charged particles in condensed phases, might it be in equilibrium conditions, or reactions on interface or in the bulk of the phase. This reasonable definition of electrochemistry includes redox processes and acid-base reactions in the bulk of solutions, which have fallen out from the modern exposition of electrochemistry for accidental historical reasons”*¹⁻³

The projects presented in this thesis, as summarized in the abstract, are multi-disciplinary but are nevertheless, have a core in electrochemistry. This chapter serves to introduce some essential and fundamental concepts of electrochemistry, forming the building-blocks of subsequent chapters. The concepts discussed herein are well-developed in most seminal modern textbooks.^{4, 5} Topics included in this chapter are electrochemistry at equilibrium, electrode kinetics and mass transport. Moreover, the practical aspects of electrochemistry such as the use of a three-electrode system, size of the working electrodes and various voltammetric techniques are also discussed.

1.1 Electrochemistry at Equilibrium

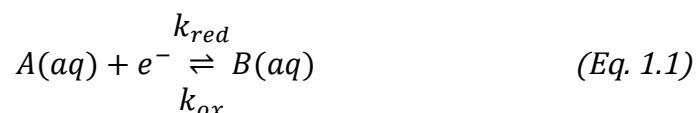
In analytical electrochemistry, the most interesting chemical reactions are those resulting in a flow of Faradaic currents at an electrode-solution interface. For the current to flow in electrochemical cells, it needs a minimum of *at least* two electrodes, connected via an

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external circuit, and immersed in a solution containing redox-active chemical species and, usually, an inert electrolyte. Such electrochemical reactions leading to a current flowing in the circuit can be broadly classified as either, *galvanic* or *electrolytic* cells. The chemical reactions occurring at the electrode interface of the former, a *galvanic cell*, is spontaneous and the electrochemical energy can be ‘harvested’ by an external load – such as that in a battery during discharge. The latter, namely an *electrolytic cell*, is when the circuit is connected to an external power source, perturbing the interfacial electrochemical reaction and driving the formation of the desired electrochemical products.

1.1.1 Electron Transfer at the Electrode Interface

Regardless of the type of electrochemical cell, the chemical reactions at the electrode interface are driven by the potential difference between the electrode and solution. For a simple aqueous redox-active couple involving one-electron transfer, the interfacial reaction can be described by



where k_{red} (m s^{-1}) and k_{ox} (m s^{-1}) are the heterogeneous electron transfer rate constants for the reduction and oxidation reaction, respectively. Examples of such redox couples, A/B , are $Ru(NH_3)_6^{3+/2+}$ and $Fe(CN)_6^{3-/4-}$.

Figure 1.1 shows a schematic of the interfacial reaction driven by the difference in electrochemical potential at the electrode-solution boundary. To understand the driving force, the ‘electron energy’ in the individual phases has to be considered. A useful term here is the Femi level from Fermi-Dirac statistics,^{6, 7} which is the hypothetical electron energy where the occupation probability among the various electron energy levels is one half; in other words, it can be seen as the maximum energy of the occupied electron levels

(at zero Kelvin) and represents the electrochemical potential of electrons in the phases of interest - the metal electrode ($\bar{\mu}_e^m$) and solutions ($\bar{\mu}_e^s$).^{4, 8}

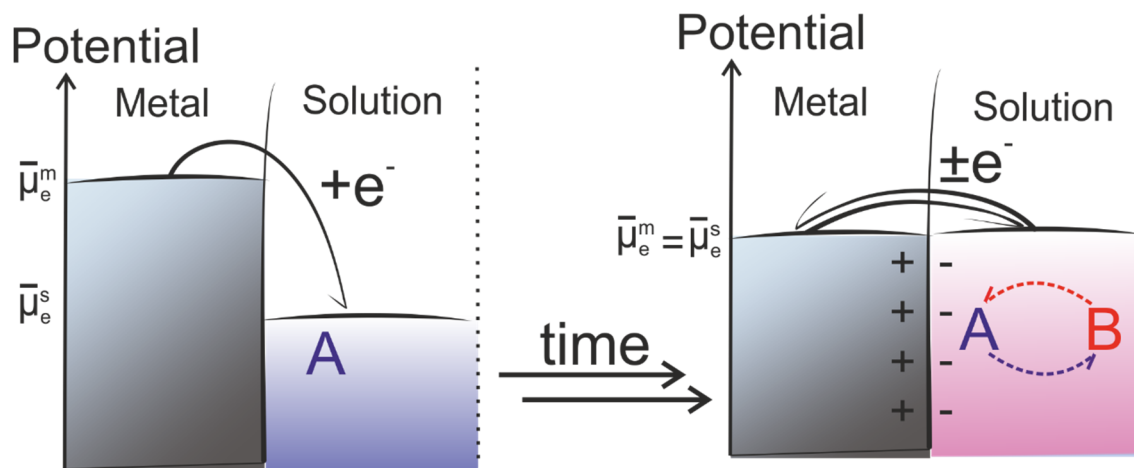


Figure 1.1. Illustration of the potential difference between an electrode and solution. $\bar{\mu}_e^m$ and $\bar{\mu}_e^s$ are the electrochemical potentials of the metal and solution phases, respectively.

First, the bonding in the metal can be approximately described by a ‘sea’ of freely moving or delocalized electrons which bind together a lattice of metal cations. This delocalization is characteristic of metallic bonds effectively form a continuum of energy levels – sometime this continuum is referred to as a ‘band’ structure’ due to the infinitesimally small spacing between adjacent energy levels - which are filled up by the finite number of electrons to an energy maximum $\bar{\mu}_e^m$, the Femi level of the metal.

The potential of the solution phase is controlled by the electronic levels of the soluble oxidized and reduced species. The electronic structures of a generic redox couple A/B in the aqueous phase, in contrast to metals, are molecular in origin and are discrete in values. Following from Equation 1.1, $A(aq) + e^- \rightleftharpoons B(aq)$, the extra electron in B is said to occupy the lowest unoccupied (or in some cases, singly occupied) molecular orbital of A . Although not shown in the schematic, this different occupancy of molecular orbitals will alter the solvation energy of the ion in solution. Hence, the electron energies of the two species have different values, even if the same molecular orbitals are involved.

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Illustrated in Figure 1.1 is a scenario where initially, the Femi level of the electrode ($\bar{\mu}_e^m$) is higher than that of the solution ($\bar{\mu}_e^s$) – which the latter only contains species A prior to electron transfer. It is thermodynamically favorable for the electrons leave the Femi level of the metal to join species A in the solution phase, lowering the energy of the system, which in turn results in a solution containing a mixture of A and B . During this progress, the Femi level of the metal decreases as the electrons occupying the metallic ‘band’ escapes into the species in solution. Conversely, the Femi level of the solution phase increases as it gains electrons. After a period of time, the system establishes electrochemical equilibrium as the Femi levels of the electrode equal to that in the solution ($\bar{\mu}_e^m = \bar{\mu}_e^s$); under this condition, the rate of the oxidation equals to that of the reversal leading to a *net-zero* in the Faradaic current.

Note that, before contacting the solution, the metal is necessary neutral. At electrochemical equilibrium, overall, the metal loses electrons to the solution phase; At the metal-solution interface, a positive charge is developed at the surface of the metal and conversely a negative charge at the solution interface. This is the physical origin of the potential difference at the electrode-solution boundary. The mathematics formulation of electrochemical potential is described in detail in the next section, which leads to the widely known Nernst equation describing electrochemistry at equilibrium.

1.1.2 Electrochemical Potential and the Nernst Equation

The concept of electrochemical potential $\bar{\mu}_i^\alpha$, for species i with z_i charge in phase α , was developed by Butler⁹ and Guggenheim^{10, 11}

$$\bar{\mu}_i^\alpha = \mu_i^\alpha + z_i F \phi^\alpha \quad (\text{Eq. 1.2})$$

where F is the Faraday constant ($96485.3 \text{ C mol}^{-1}$), ϕ^α is the potential of phase α and μ_i^α is the chemical potential

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$$\mu_i^\alpha = \left(\frac{\partial G}{\partial n_i} \right)_{T,P,n_{j \neq i}} \quad (\text{Eq. 1.3})$$

where n_i is the number of moles of species i in phase α and G is Gibbs free energy. Moreover, the chemical potential can be expressed in terms of a standard chemical potential $\mu_i^{0\alpha}$

$$\mu_i^\alpha = \mu_i^{0\alpha} + RT \ln(a_i^\alpha) \quad (\text{Eq. 1.4})$$

where R is the ideal gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T is the temperature (K) and a_i^α is the activity of species i in phase α (mol dm^{-3}). The activity of a species i is related to the concentration (mol dm^{-3}) multiplied by an ‘activity coefficient’ γ accounting for solution non-ideality.

Although the electrochemical potential of any species i in phase α , expressed in Equation 1.2, is the sum of its *chemical potential* and *electrostatic* contributions; Guggenheim in his original work has, however, concluded that “*the conception of splitting the electrochemical potential $\bar{\mu}_i^\alpha$ of an ion of type i , into the sum of a chemical term μ_i^α and an electrical term $z_i F \phi^\alpha$ is quite arbitrary and without physical significance*”.^{10, 11} This arises from the “loosely”¹² defined potential of phase α (ϕ^α), and that the single-ion activity is experimentally unmeasurable due to the interdependent liquid junction potential.^{10, 11} The measurement and physical significance validity of the latter (single-ion activity) has been debated over the past century, a brief historical perspective of this heated debate,¹² and more recent discussions can be found elsewhere.^{13, 14} Nevertheless, the work in this thesis concerns the electrochemical potential of more than one phase, involving more than one species, in which the potential difference arises from linear combinations of Equation 1.2 (directly below) which is entirely experimentally measurable.¹¹

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At electrochemical equilibrium, the sum of the electrochemical potential of all species involved in the equilibrium determining reaction is zero. For the generic redox couple given in Equation 1.1

$$\bar{\mu}_A^s + \bar{\mu}_e^m = \bar{\mu}_B^s \quad (\text{Eq. 1.5})$$

$$(\mu_A^s + z_A F \phi^s) + (\mu_e^m - F \phi^m) = (\mu_B^s + z_B F \phi^s) \quad (\text{Eq. 1.6})$$

Realising $z_A - z_B$ equals to 1, Equation 1.6 rearranges to

$$\phi^m - \phi^s = \frac{\mu_A^s + \mu_e^m - \mu_B^s}{F} \quad (\text{Eq. 1.7})$$

Substituting Equation 1.4 into Equation 1.6 and 1.7, and an early form of the Nernst equation can be obtained^{4, 8}

$$\phi^m - \phi^s = \frac{\Delta\mu^0}{F} + \frac{RT}{F} \ln \left(\frac{a_A}{a_B} \right) \quad (\text{Eq. 1.8})$$

where $\Delta\mu^0 = \mu_A^{0s} + \mu_e^{0m} - \mu_B^{0s}$. In practice, however, the absolute value of electrode potential ($\phi^m - \phi^s$) at an electrode-solution interface cannot be measured; the measurement is obtained with at least *two* electrode-solution interfaces for a complete circuit, more of which is discussed in Section 1.4.1. A second electrode must be used as a reference electrode and can be treated exactly as above. The components of the reference electrode are typically at either a standard or a saturation concentration such that the components remain unchanged during the experiment with a small amount of current ($< \mu\text{A}$) passed through the reference electrode is ensure this constancy of composition. This give rise to the overall expression

$$(\phi^m - \phi^s)_{\text{working}} - (\phi^m - \phi^s)_{\text{reference}} = \frac{\Delta\mu_{\text{working}}^0}{F} + \text{constants} + \frac{RT}{F} \ln \left(\frac{a_A}{a_B} \right) \quad (\text{Eq. 1.9})$$

where the term *constants* arise from the chemical potentials and constant concentrations at the reference electrode. Examples of commonly used reference electrodes are the

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normal hydrogen electrode (NHE) and the *saturated calomel electrode* (SCE). This leads to

$$E = E^0 + \frac{RT}{F} \ln \left(\frac{a_A}{a_B} \right) \quad (\text{Eq. 1.10})$$

where E is potential measured against the reference electrode (NHE or SCE) and $E^0 = \frac{\Delta\mu_{\text{working}}^0}{F} + \text{constants}$. However, employing solutions of unit activity in electrochemical systems is often impractical (or impossible if the activity coefficients are unknown) as the activity depends strongly on the concentration of the reactants and other electrolytes present.

As a generalization, the formal potential E_f^0 is introduced to allow voltammetry measurements without knowledge of the activity coefficients and extend the practicality beyond the standard condition. The IUPAC definition of the formal potential E_f^0 is:¹⁵

“[The] Conditional (formal) potential, $E_c^{0'}$, is related to the potential of a cell reaction, E_{cell} , by an equation analogous to that relating E_{cell} to the standard potential E_0 , with the activity, a_i , replaced by any composition variable, c_i (to be indicated by a subscript). For

example: $E_{\text{cell}} = E_c^{0'} - \frac{RT}{nF} \sum_i \nu_i \ln c_i$.”

Adopting the notations used in this thesis, the expression above becomes:

$$E = E_f^0 + \frac{RT}{F} \ln \left(\frac{c_A}{c_B} \right), \text{ where } E_f^0 = E^0 + \frac{RT}{F} \ln \left(\frac{\gamma_A}{\gamma_B} \right) \quad (\text{Eq. 1.11})$$

Thus, we arrive at the final, and the most accessible, form of the Nernst equation for a generic aqueous redox couple. Since the Nernst equation describes the electrochemical reaction at equilibrium, the rate of the forward reaction equals to that of the backward reaction, thus no kinetic information regarding k_{red} and k_{ox} are provided.

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In dynamic electrochemistry, however, a potential more positive or negative than the cell potential is applied, so as to perturb and results in non-equilibrium at the electrode-solution interface. By altering the applied potential E with time, the direction and rate of the electrolysis can be controlled and calculated from the measured current. The next section gives insight into the electrode kinetics in the event of electrochemical disequilibrium.

1.2 Electrode Kinetics

In dynamic electrochemistry, the potential E applied to an electrode of interest relative to a reference electrode (see above) varies with time in such a way to deliberately perturbate the electrochemical equilibrium at the interface of interest. Under these conditions, the flux of reactant j ($\text{mol cm}^{-2} \text{ s}^{-1}$) undergoing electrolysis at a (macro)electrode is directly proportional to the measured current I

$$I = nFAj \quad (\text{Eq. 1.12})$$

where n is the number of electrons transferred per reaction and A is the geometric area of the electrode. Note that, the linear relationship between current I and flux j in Equation 1.2 assumes a uniform flux j over the geometry area of the electrode. (This assumption is true for macro-sized electrodes where the geometric area is significantly larger than the diffusion layer thickness but breaks down when the electrode is microns in size – more of which in Section 1.4.2).

The uniform flux j can be considered as the *net* rate of heterogeneous reactions at the electrode-solution interface, analogous to the rate of a homogeneous chemical reaction dc_j/dt . The rate for the interfacial reactions (for the A/B redox couple in Equation 1.1) is given by:

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$$j = -D_A \left(\frac{\partial c_A}{\partial x} \right)_{x=0} = -[k_{red}c_{A,0} - k_{ox}c_{B,0}] \quad (Eq. 1.13)$$

where k_{red} and k_{ox} has units of cm s^{-1} . The subscript '0' corresponds to the surface concentration, which in reality, corresponds to within the tunnelling distance of $\sim 10 - 20$ Å from the electrode surface.

The interfacial rate constants, k_{red} and k_{ox} , are most frequently described by Butler-Volmer kinetics, which sometimes is referred to as Ergey-Gruz-Volmer kinetics. It was developed independently first by Butler in the UK in the late 1920s, then by Ergey-Gruz and Volmer in 1930, who introduced the notion of the transfer coefficient into Butler's work published a decade earlier.¹⁶⁻¹⁸ The development of this theory assumes the energy of the transition state, in respect to its potential dependence, lies between those of the products and reactants.^{4, 8} The activation energies for the electron transfer reaction are derived, producing the following Arrhenius type expression for the rate constants:

$$k_{red} \propto e^{-\frac{\alpha F}{RT}(E)} \quad (Eq. 1.14)$$

$$k_{ox} \propto e^{\frac{(1-\alpha)F}{RT}(E)} \quad (Eq. 1.15)$$

where α is the transfer coefficient introduced by Ergey-Gruz and Volmer, and takes the value between zero and one for a simple one-electron transfer. If α is close to zero, the transition state is reactant-like for a reduction, whilst the transition state is product-like if α is near unity.

Using the formal potential E_f^0 as defined by the IUPAC (shown in Equation 1.11), Butler-Volmer kinetics is more conveniently expressed relative to the standard formal potential $(E - E_f^0)$ giving rise to

$$k_{red} = k_0 e^{-\frac{\alpha F}{RT}(E - E_f^0)} \quad (Eq. 1.16)$$

$$k_{ox} = k_0 e^{\frac{(1-\alpha)F}{RT}(E - E_f^0)} \quad (Eq. 1.17)$$

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where k_0 is the standard electrochemical rate constant. Substituting Equation 1.16 and 1.17 into Equation 1.13 gives

$$j = -D_A \left(\frac{\partial c_A}{\partial x} \right)_{x=0} = -k_0 \left[e^{-\frac{\alpha F}{RT}(E-E_f^0)} c_{A,0} - e^{\frac{(1-\alpha)F}{RT}(E-E_f^0)} c_{B,0} \right] \quad (Eq. 1.18)$$

It can be seen from the above expressions that, the interfacial rate constants k_{red} and k_{ox} are extremely sensitive to the applied potential; an over-potential η ($E - E_f^0$) of only 200 mV increases the rate constant by a factor of ca. 50.

The next section concerns the mass transport of materials to and from the electrode in response to an electrochemical perturbation.

1.3 Mass Transport

In dynamic electrochemistry the surface concentration of the reactant $c_{A,0}$ is perturbed from equilibrium by the applied potential; it is evident that $c_{A,0}$ is different from the bulk:

$$c_{A,0} \neq c_{A,bulk} \quad (Eq. 1.19)$$

Understanding the mass transport of materials is prerequisite to all analysis in electrochemistry as it, in almost all electrochemical systems, has a significant role in the measured Faradaic current. In the absence of convection, such as that due to temperature differences or mechanical stirring,¹⁹ and with sufficient supporting electrolyte to shield the charged species from the electric field,²⁰ the mass transport of materials to and from the electrode surface is driven solely by the concentration differences. The diffusional flux j in one-dimensional is described by Fick's first law of diffusion:^{21, 22}

$$j = -D \frac{\partial c}{\partial x} \quad (Eq. 1.20)$$

The negative sign states that diffusion takes place down the concentration gradient. Moreover, the temporal evolution of the concentration c at a point of x is described by Fick's second law of diffusion:

$$\frac{\partial c}{\partial t} = D \left(\frac{\partial^2 c}{\partial x^2} \right) \quad (\text{Eq. 1.21})$$

which follows from the 1st law via conservation of mass. The diffusion coefficient D has units of m^2s^{-1} . The equation above is one dimensional. In three dimensional, this becomes:

$$\frac{\partial c}{\partial t} = D \nabla^2 c = D \left(\frac{\partial^2 c}{\partial x^2} + \frac{\partial^2 c}{\partial y^2} + \frac{\partial^2 c}{\partial z^2} \right) \quad (\text{Eq. 1.22})$$

The distance over which the bulk concentration is perturbed by the interfacial reaction can be approximated by the effective diffusion layer thickness δ ; introduced by Nernst and is commonly known as the ‘Nernst diffusion layer’.²³ Figure 1.2 illustrates the concentration profile of the reactant during an electrolysis reaction. The value of diffusion layer thickness δ is the distance at which the tangent of the interfacial concentration profile coincides with the bulk concentration, illustrated with blue dotted lines.

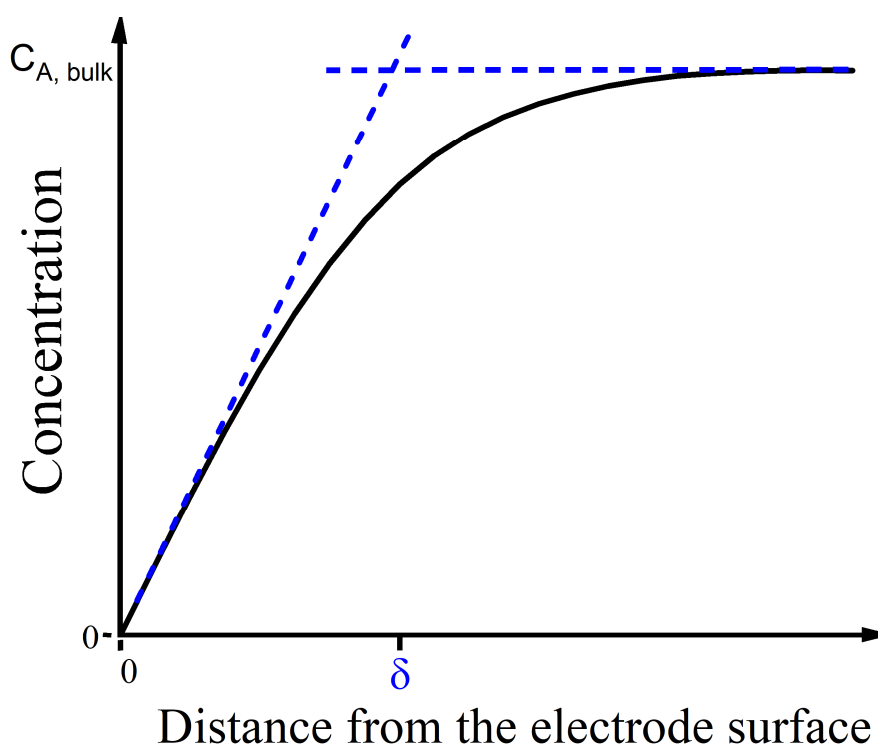


Figure 1.2. Instantaneous concentration profile depicting the depletion of the reactant on a planar electrode. Black line – Concentration profile of analyte. Blue line – The diffusion layer thickness approximation.

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On the basis of Figure 1.2 the interfacial concentration gradient $\left(\frac{\partial c}{\partial x}\right)_{x=0}$ multiplied by the diffusion layer thickness δ is used to approximately give the bulk concentration.

$$\left(\frac{\partial c}{\partial x}\right)_{x=0} \delta \approx c_{A,bulk} \quad (\text{Eq. 1.23})$$

The interfacial flux j of a macro-disk electrode, in a chronoamperometry experiment, is described by the Cottrell equation (more formally discussed in Section 1.4.3)

$$j = -D \left(\frac{\partial c}{\partial x}\right)_{x=0} = -\frac{\sqrt{D} c_{A,bulk}}{\sqrt{\pi t}} \quad (\text{Eq. 1.24})$$

Substituting Equation 1.23 into Equation 1.24, the perturbation distance from the surface of a macro-electrode, to a good approximation, can be described by the distance δ :²⁴

$$\delta \approx \sqrt{\pi D t} \quad (\text{Eq. 1.25})$$

From Equation 1.25, a diffusion layer thickness on the orders of 100 μm of magnitude can be estimated, for a typical experiments timescale of tens of seconds and using a typical diffusion coefficient of $10^{-9} \text{ m}^2 \text{ s}^{-1}$. Note that, estimating the diffusion layer thickness using the interfacial concentration gradient as above only crudely approximates the actual concentration profile (Figure 1.2), but this nevertheless, provides a quick “back-of-the-envelope” calculation to the extent of depletion zone – to well within the correct order of magnitude.

The focus of the next section turns to discuss the commonly deployed electrochemical methods used in electrochemical experiments.

1.4 Electrochemical Methods

Now that some of the most fundamental physicochemical processes occurring in electrochemical systems have been introduced, this section seeks to discuss and explain the logic and theory behind the electrochemical set ups commonly used in analytical

electrochemistry, such as the use of a three-electrode system, macro- or micro-electrodes, and electrochemical methods such as cyclic voltammetry and chronoamperometry.

1.4.1 Three-electrode System

In addition to the two electrodes discussed above, namely the working and reference electrodes, a third electrode - commonly known as the '*counter*' electrode - is used in conjunction with the other two for electrode kinetic studies. The three-electrode system is controlled by a computer-managed potentiostat.

During a typical voltammetric experiment, the potentiostat applies a potential E to the working electrode, relative to the reference electrode:

$$E = (\phi_m - \phi_s)_{working} - (\phi_m - \phi_s)_{reference} - IR_u \quad (Eq. 1.26)$$

where $\phi_m - \phi_s$ is the potential drop (V) at the electrode-solution interface and which drives the working electrode reaction of interest. The sole purpose of the reference electrode is to provide a *constant* potential, $(\phi_m - \phi_s)_{reference}$, to allow the measurement. As each Faradaic current induces an electrolysis process, there must be transfer of electrons across the electrode interface; for a SCE this could self-defeating if a two-electrode system were used and large currents drawn through the reference electrode; this will likely shift the referencing potential during the experiments and the potential at the working electrode becomes unknown and time dependent. To solve this problem, a counter electrode, which is typically an inexpensive graphite rod, is introduced so the current flows between this electrode and the working electrode. This significantly reduces the current, almost to zero, drawn by the reference electrode, and thus any chemical changes in its delicate and precise composition. Therefore, the only current drawn through the reference electrode is to measure the potential of the cell, so that the term ($V = IR$) in the above equation becomes more effectively close to zero (but see below). This three-electrode set up can render the chemical composition of the reference

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electrode essentially unchanged during an electrochemical experiment while high currents at the working electrode are measured continuously over long periods. Given that the reference electrode is fixed and the IR term minimized the three-electrode approach allows a controlled change in the driving force of the electrode reaction, viz, $\phi_m - \phi_s$ is to be applied to the working electrode; Equation 1.26 shows that then a change of say 1V in E results in a corresponding change in the driving force.

As current flows between the working and counter electrodes, the medium which the two electrodes bathed in will develop an ‘ohmic potential drop’ (IR_s); this is unavoidable as a fraction of the applied potential is used to drive the ionic current in a non-zero resistance solution. The advantage of using the three-electrode setup is that the reference electrode, from which potentials are measured relative against, can be placed near to the working electrode in such a way that only a fraction of this ohmic drop, termed *uncompensated resistance*, appears in Equation 1.26 as IR_u (where $R_u < R_s$).⁸ Noting this potential issue, the results presented in this thesis use sufficient electrolyte of at least 0.1M so as to minimize R_u . Therefore, the contribution of IR_u towards potential difference of the cell can be assumed insignificant.

1.4.2 Macro- and Micro-electrodes

The ‘party-piece’ in this three-electrode system has to be the working electrode, as ultimately, it is the electrochemical interactions occurring at this electrode-solution interface that are being measured and recorded by the computer-controlled potentiostat. The reference and counter electrodes are there merely to facilitate and to support the measurements. There are a vast number of variables when it comes to choosing the optimum working electrode(s) for an experiment, for example, the electrode materials, the shape and size of it, and not to mention the wealth of different possible modifications

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to the electrodes. Choosing an optimum working electrode largely depends on what information one wants to extract from the electrochemical system, it is less trial-and-error, but more like sculpting a work-of-art which require the right tool at the right time. For many, but not all, electrochemical reactions involving the transfer of electrons, the working electrode solely serves as an inert electrical conductor and does not appear in the rate-determining step of the reaction under study. In this section, the focus resides in the effect of the geometric size of the working electrode and associated physicochemical factors. As discussed in Section 1.3, the distance at which the solution is perturbed by the interfacial reaction is on the orders of magnitude of 100 μm . Thus, generally, the working electrodes are classified into two categories: macro- and micro-electrode.²⁵ The former, macro-electrodes are commonly disc-shaped (however the shape is unimportant in this category, see below) and have radii $r_e > 1\text{mm}$ which is larger than the Nernst diffusion layer thickness ($r_e \gg \delta$). The disc-shaped micro-electrode, or commonly referred to as ‘micro-disc electrode’, has a radius less than 50 μm which is less than the Nernst diffusion layer ($r_e \ll \delta$).²⁵

Figure 1.3 is a schematic showing the macro- and micro-electrode during a typical electrochemical experiment. The purple shade depicts the Nernst diffusion layer (of the reagent) relative to the geometric size of the electrodes. The arrows represent the magnitude and direction of the diffusive flow vectors in the vicinity of the electrodes. The important contrast between macro- and micro-electrodes are the different diffusion regimes in operation during the electrochemical experiments. Since the geometric area of the macro-electrode is much bigger than that of the diffusion layer (δ), the depletion zone is said to be ‘confined’ to the surface and, to a good approximation, the diffusional flux is one-dimensional and homogeneous across the surface. On the other hand, for micro-disc electrode, the diffusion layer (δ) expands far beyond the electrode – this leads to

convergent diffusion where the flux j is heterogeneous from the edge of the electrode to the center.

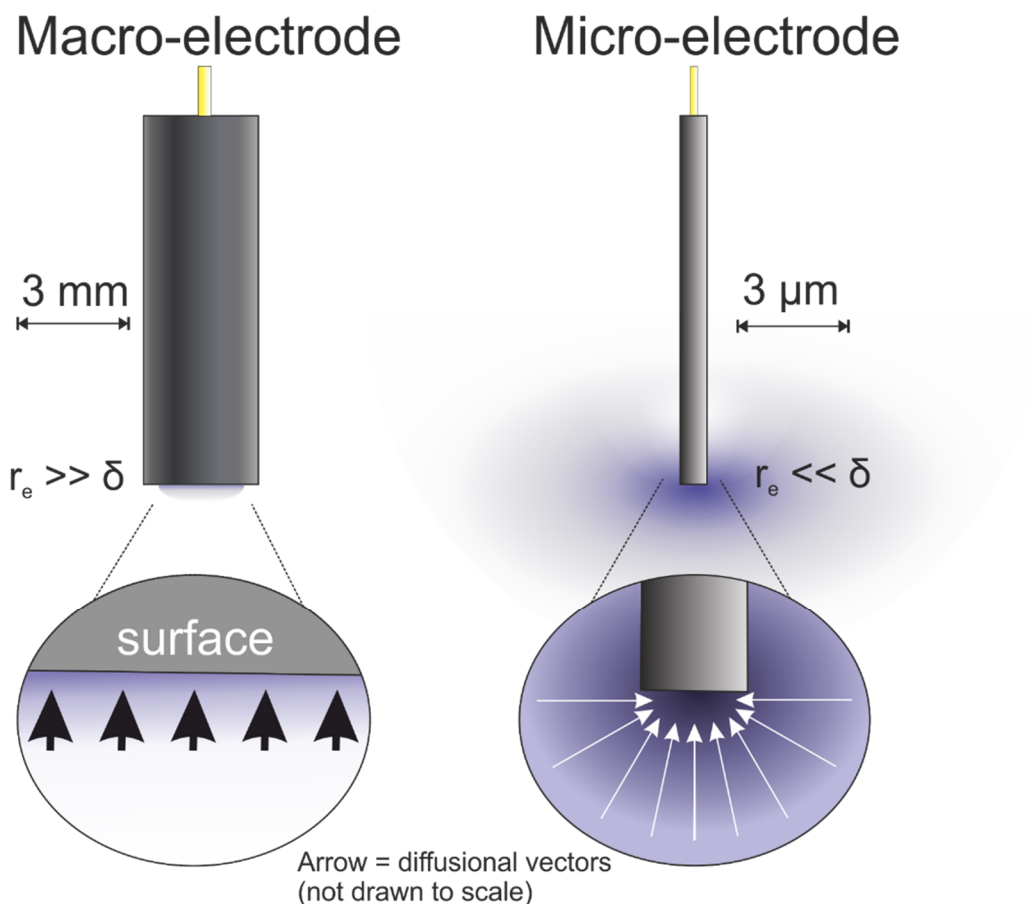


Figure 1.3. A schematic depicting the size of the macro- and micro-electrode relative to the length scale of the Nernst diffusion layer thickness (δ). On the left is a macro-electrode under linear diffusion regime ($r_e \gg \delta$). On right, convergent diffusion regime is operating at the micro-electrode ($r_e \ll \delta$). The arrow are vectors depicting the direction of the diffusional flux of reactants.

In terms of the shape of the macro-electrode, it can be deduced from above that, is unimportant as long as the geometric area is sufficiently large such that convergent contribution from the edges is small compare to the dominating linear diffusion. This results in the direct proportionality of the current to the geometric area of the electrode ($I = nFAj$, Equation 1.12).

For the microelectrodes, however, the flux of material j at the edge of the electrode is much higher than the centre due to convergent diffusion. The main difference here is that convergence diffusion is three-dimensional, as opposed to one-dimensional in the case of

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linear diffusion. Since flux j dominates at the edge of the micro-electrode, the flux is now proportional to the radius of the micro-disc electrode r_e (as is the circumference of a circle). The analytical expression of Faradaic currents on a micro-disc electrode is discussed in the next section.

Another consideration in choosing the size of the working electrode is that the magnitude of the undesired capacitive current I_{cap} which scales with the absolute area of the electrode (irrespective of the size)

$$I_{cap} = 2AC\nu \quad (Eq. 1.27)$$

where C is the capacitance ($\mu\text{F cm}^{-2}$) of the electrode assumed in the above to be potential independent and ν is the scan rate (Vs^{-1}). The capacitive current arises from double-layer charging of an electrode-solution interface, analogous to that of a capacitor.⁸

Ultimately, there is no definite answer in choosing the geometric area of the working electrode, and it is important to realize in analytical electrochemistry that the diffusion regime in operation (linear or convergent) provides different information about the same electrochemical system, especially when subsequent chemical reactions are involved.²⁶ It is worth noting that the fabrication of nano-electrodes is possible with benefits that further amplifies those discussed herein for micro-electrodes.^{27, 28}

1.4.3 Chronoamperometry

Chronoamperometry is a simple but elegant voltammetric technique where a ‘potential step’ is applied to the working electrode with the current measured over time. Figure 1.4 shows the potential step from an initial potential E_1 , at which there is no reaction of interest, to an over-potential E_2 so that the reaction becomes instantaneously ‘fully driven’. The initial potential E_1 is chosen where negligible Faradaic current flows and the

over-potential ($\eta = E - E_f^0$) is typically atleast ~ 200 mV in excess of the formal potential E_f^0 of the analyte. Thus, the concentration of the analyte at the electrode interface is completely depleted upon the potential step, not limited by the electron transfer kinetics.

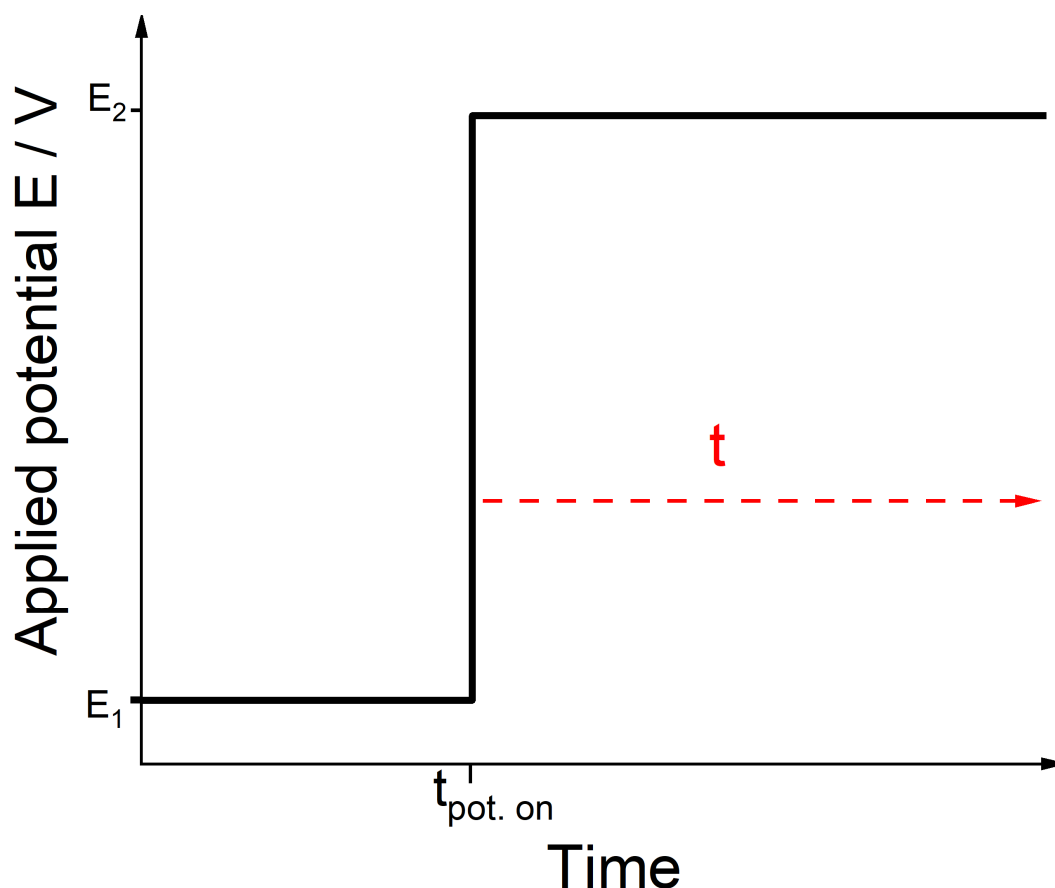


Figure 1.4. The potential applied as a function of time in a chronoamperometry experiment.

For a macro-electrode with a radius of ≥ 1 mm, the diffusion of the analyte to the electrode surface is predominantly linear. As discussed in Section 1.3, the Nernst diffusion layer (δ) ~ 100 μm , within tens of seconds of the experiment, is much smaller than the geometric area of a macro-electrode. Hence the diffusion profile of a macro-electrode is generally one-dimensional.

In 1902, the problem of ‘potential step chronoamperometry’ for a macro-electrode was solved by Frederick G. Cottrell.²⁹ Fick’s second law of diffusion (Equation 1.21) was

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solved by recognizing that, $c_{A,0} = 0$ and $c_{A,\infty} = \text{bulk}$ since the potential step. Cottrell derived the the following expression, bearing his name, describing how the chronoamperometric current I evolves with time t :

$$I_{\text{Cottrell}} = -\frac{nFA\sqrt{D}c^*}{\sqrt{\pi t}} \quad (\text{Eq. 1.28})$$

where t (s) is the time relative to $t_{\text{pot.on}}$. The Cottrell equation predicts that, for a one-dimensional diffusion problem, the current tends to zero when the time approaches infinity. In practice, natural convection may inevitably arise during the experiment as the solvation shell of the redox products, formed at the electrode interface, can be different to that of the reactant in bulk, causing a density gradient-driven convection as the diffusion layer thickness δ increases with time. Thus, leading to slightly higher current than that predicted by the Cottrell equation at a long time ($t > 60\text{s}$).¹⁹

The chronoamperograms obtained on a micro-disc electrode, however, is more complex. As mentioned, the radius of the electrode is much smaller than the diffusion layer thickness within tens of seconds of experiment ($r_e \ll \delta$). The radius r_e is obviously a constant during the experiment, but the Nernst diffusion layer thickness is time-dependent ($\delta(t) \approx \sqrt{\pi Dt}$). With the modern potentiostats capable of achieving sampling frequency of 10^5 Hz, a chronoamperogram contains *both* diffusion regimes, linear at short times ($< 200 \mu\text{s}$) and convergent diffusion at a significantly longer time (few seconds), can be obtained on a micro-disc electrode of radius of a few microns. Figure 1.5 shows such a chronoamperogram where an overpotential η at $t = 0$ is applied to fully drive a redox reaction.

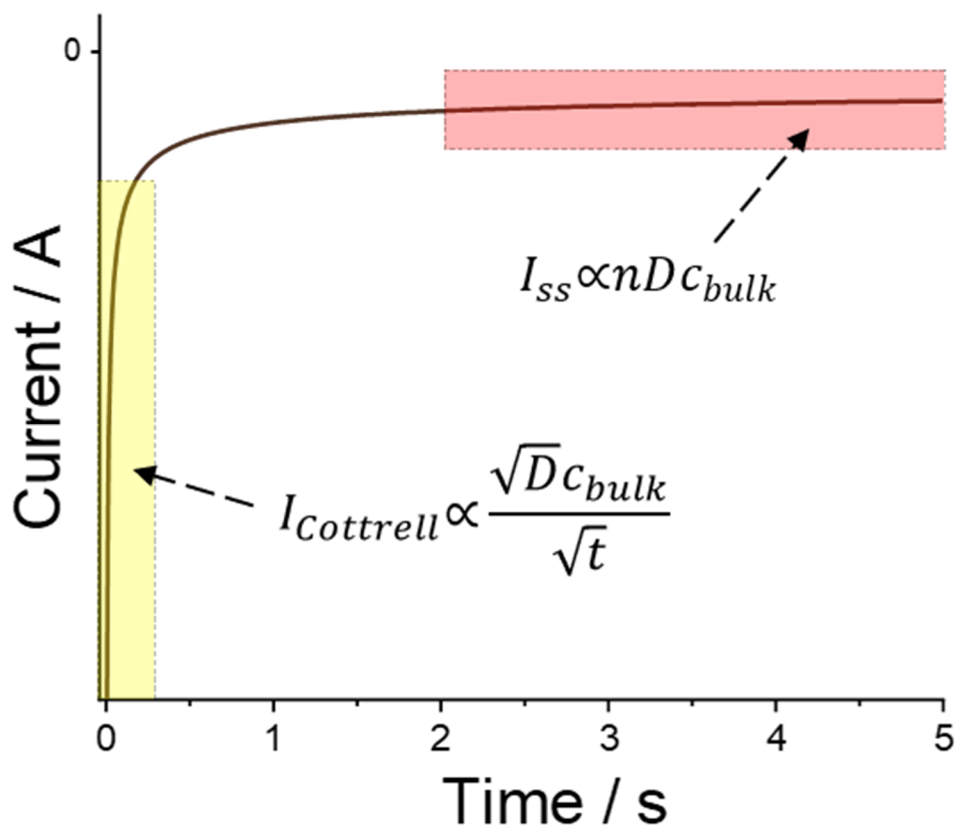


Figure 1.5. Current decay in a chronoamperometry experiment for the reduction of $A + e^- \rightarrow B$ on a micro-disc electrode.

At short times, the current decay is described by the Cottrell equation (1.28), which is inversely proportional to $\sqrt{t}$. However, it starts to deviate from the Cottrell equation when time $t \approx \frac{r_e^2}{\pi D}$, as the diffusion layer thickness is comparable to the radius of the electrode.

The reason is that the Cottrell equation is derived for one-dimension diffusion profile, whereas convergent diffusion has contributions from three dimensions. Consequently, in contrast to a macro-electrode where the current approaches zero, a micro-disc electrode gains additional convergent flux at the edge of the electrode, sufficient to compensate the consumption of analyte and therefore a steady-state current I_{ss} is established

$$I_{ss} = -4nFDc_{bulk}r_e \quad (Eq. 1.29)$$

The analytical expression describing the full current-time transient on a micro-disc electrode is developed by Shoup and Szabo:³⁰

$$I = -4nFDc_{bulk}r_e f(\tau) \quad (Eq. 1.30)$$

where $f(\tau) = 0.7854 + 0.8863\tau^{-\frac{1}{2}} + 0.2146 \exp\left(-0.7823\tau^{-\frac{1}{2}}\right)$ and $\tau = \frac{4Dt}{r_e^2}$

When $\tau \rightarrow \infty$, Equation 1.30 reduces to Equation 1.29. Therefore, by virtue of substitution or line of best fit, D and either n or c_{bulk} of the analyte can be simultaneously obtained in a single chronoamperometry experiment using a micro-electrode, providing the third parameter is known.

1.4.4 Cyclic Voltammetry

Cyclic voltammetry is the ‘bread and butter’ voltammetric technique in electrochemistry.

“Without bread all is misery”, William Cobbett

“There is not a thing that is more positive than bread”, Fyodor Dostoevsky

“Cyclic voltammetry is the bread of life”, Richard Compton

As given by the name, in cyclic voltammetry the applied potential is varied during the experiment and the resulting current is measured. Shown in Figure 1.6 a) is the triangular potential waveform used in cyclic voltammetry.

Let us consider a simple redox couple, $A + e^- \rightleftharpoons B$, where only species A is initially present in the solution. The applied potential is swept linearly from E_1 to a second potential E_2 , and then reversed to form the triangular waveform; it can be viewed as two back-to-back linear sweep voltammograms with equal and opposite voltage scan rate (Vs^{-1}), commonly referred to as the *forward* and *backward sweeps*.

The voltammogram plots the recorded current versus the applied potential. The starting potential E_1 is normally selected so that negligible Faradaic current is observed, and E_2 is normally in excess of the formal potential E_f^0 of the redox couple A/B .

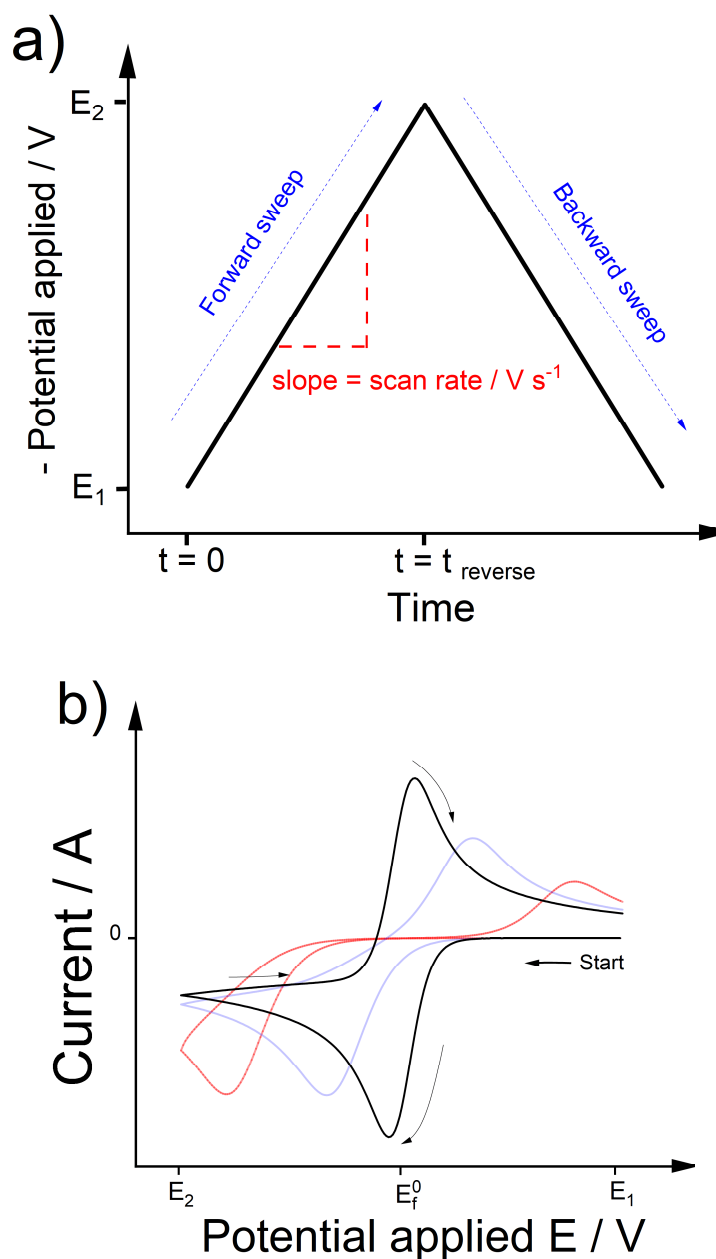


Figure 1.6 a) The triangular potential waveform of the cyclic voltammetry experiment. b) Cyclic voltammogram for the redox couple, $A(aq) + e^- \rightleftharpoons B(aq)$, recorded on a macro-electrode; the black, blue and red line represent reversible, quasi-reversible and irreversible electrochemical kinetics k^0 respectively.

Figure 1.6 b) illustrates the voltammograms obtained on macro-electrodes over a range of different levels of electrochemical reversibility of the A/B redox couple. During the forward sweep, as the potential sweeps from the initial potential E_1 , the current increases with the rate constant k_{red} following Equation 1.16. As a result, the interfacial concentration of A is rapidly consumed and concurring mass transport of A from the bulk

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solution to the electrode interface - down the concentration gradient - in response to the interfacial concentration changes. Initially this is fast but as the diffusion layer thickness increases the linear diffusion becomes insufficient to match that of the rate of depletion at the surface, this results in a peak-shaped current-potential response as the surface concentration of species A is near zero or depletes, causing the subsequent current to decay in a Cottrellian manner, inversely to $\sqrt{t}$.

Also shown in Figure 1.6 b) are voltammograms with different standard electrochemical rate constant (k^0), with increasing irreversibility or slower electrode kinetics from black to red line. Most notably, the size of the peak current decreases while the peak-to-peak separation ΔE_{pp} is increased. The term fast (reversible) or slow (irreversible) electrode kinetics in electrochemistry refers to the comparison between the standard electrochemical rate constant (k^0) and the mass transport coefficient (m_T):

$$k^0 \gg m_T ; \text{Reversible}$$

$$k^0 \ll m_T ; \text{Irreversible}$$

$$\text{where } m_T \sim \frac{D}{\delta} \approx \sqrt{\frac{D}{RT/Fv}} \quad (\text{Eq. 1.31})$$

Note that both k^0 and m_T has the same units (m s^{-1}). This classification was first introduced by Matsuda and Aysbe in terms of the parameter Λ .³¹

$$\Lambda = \frac{k^0}{\left(\frac{FDv}{RT}\right)^{1/2}} = \begin{cases} \Lambda \geq 15; \text{Reversible} \\ 15 \geq \Lambda \geq 10^{-3}; \text{Quasi-reversible} \\ \Lambda \leq 10^{-3}; \text{Irreversible} \end{cases} \quad (\text{Eq. 1.32})$$

It is evident from Equation 1.31 that the mass transport coefficient (m_T) of analytes increases with the scan rate (v). Therefore, since k^0 is independent of the scan rate, one expects the shape of the voltammogram to changes with an increase in the degree of irreversibility as scan rate (v) increases. Moreover, implicitly expressed in Equation 1.31, the Nernst diffusion layer thickness (δ) decreases with the increase of scan rate (v).

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As the diffusion layer thickness (δ) decreases, the instantaneous flux j at the interfacial must increases. Thus, with everything else the same, the magnitude of the measured current I is expected to increase with ν .

The relationship between the peak current I_p in the voltammogram with scan rate ν on a macro-electrode is described by the Randles-Ševčík equation for a n electron transfer reaction (such as $A + ne^- \rightleftharpoons B$):^{32, 33}

$$I_p = 2.69 \times 10^5 n^{3/2} AD^{1/2} c_{bulk} \nu^{1/2} \quad \text{at } 298K \quad (\text{reversible}) \quad (\text{Eq. 1.33})$$

$$I_p = 2.99 \times 10^5 n(n' + \alpha)^{1/2} AD^{1/2} c_{bulk} \nu^{1/2} \quad \text{at } 298K \quad (\text{irreversible}) \quad (\text{Eq. 1.34})$$

where n is the overall number of electrons transferred, n' the number of electrons transferred before the rate-determining step and α is the transfer coefficient and the other symbols have been defined previously.

The main difference between the reversible and irreversible redox couple on a macro-electrode is the peak-to-peak separation ΔE_{pp} . In the reversible limit, the ΔE_{pp} is approximately $\frac{57}{n}$ mV at 298K, where n is the number of electrons transferred in the simple redox couple (A/B). Moreover, ΔE_{pp} is independent of the scan rate in the fully *reversible* limit. Under quasi- and irreversible conditions, however, the ΔE_{pp} is significantly larger and increases with scan rate.

This can be explained with the Butler-Volmer kinetics, as shown in Equation 1.16 and 1.17; slow electrode kinetics (small k^0) requires a higher over-potential η to achieve the same electrochemical rate constant k_{red} compared to faster electrode kinetics with a higher k^0 . Thus, as can be seen in the voltammograms shown in Figure 1.6 b) for macro-electrode, and also Figure 1.7 for micro-electrodes, a higher overpotential is required to drive the reaction with a sluggish k^0 .

In the case of the voltammogram obtained with a micro-electrode, shown in Figure 1.7, the cathodic currents initially increase with the applied potential before reaching a steady-state. It does not give rise to a peak, in direct contrast to the macro-electrode due to the far more ‘efficient’ convergent diffusion. It is, however, worthwhile noting that in the limit of a pathologically fast voltage scan rates (typically 10^6 Vs^{-1}) peak-shaped voltammograms can be seen with micro-electrodes.^{34, 35} This is because the electrolysis finishes so quickly that the Nernst diffusion layer is confined to very near the surface of the micro-electrode and linear diffusion regime dominates in the timescale of those experiments.

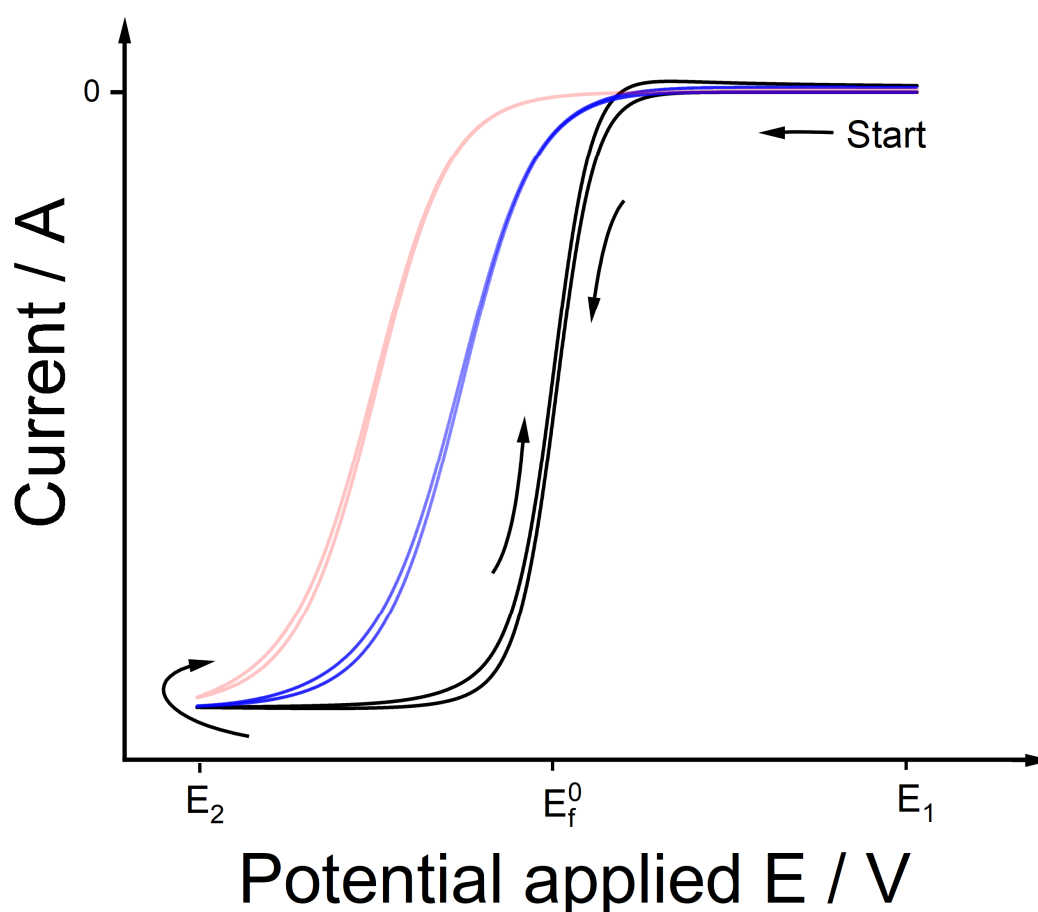


Figure 1.7 Cyclic voltammograms for micro-disc electrode are shown for different electrochemical kinetics. The redox couple in concern is $A(aq) + e^- \rightleftharpoons B(aq)$, where initially only $A(aq)$ is present in solution. The black, blue and red represent reversible, quasi-reversible and irreversible electrochemical kinetics k^0 respectively.

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Chapter 2 Electrochemistry of Insoluble Particles

Electrochemistry of *dissolved* organic and inorganic compounds is well-developed and documented across wide range of textbooks.^{1, 2} In contrast, electrochemical analysis on solids was faced with many challenges implicit in a quote from Scholz in 1992: “...[the] problems involved are severe and success was rather rare...”.³ In this Chapter, a new carbon black and polyvinylidene fluoride (PVDF) containing composite material capable of facilitating the redox chemistry of aqueous insoluble solids, over a wide range of potential window, is introduced and characterised first with three well-known redox couples. Subsequently, the study extends to insoluble mercury based mineral, red cinnabar (α -HgS), leading to a publication in *Chemistry-A European Journal*.⁴

The carbon black and polyvinylidene fluoride (PVDF) composite methodology was subsequently adopted in collaboration with Dr Bertold Rasche, (now former) RGC group member, to navigate across the full phase width of a superconductor β -Fe_{1+x}Se electrochemically using electrochemical X-ray diffraction experiments at the Diamond Light Source. This led to a VIP communication published in *Angewandte Chemie International Edition*.⁵ Section 2.3.3 will highlight the electrochemistry behind the post-synthesis manipulation of β -Fe_{1+x}Se, across the full phase width of x, facilitated by the carbon/PVDF composite. The contributions from all co-authors are fully acknowledged in Section 2.3.3.

The carbon-composite methodology discussed in this chapter is generic for all aqueous insoluble solids. The scientific outcomes shown in this chapter, especially the in situ X-ray diffraction showcase experiment, provides a sound alternative and extension to the existing solid-state electrochemical methodologies. Reuse permissions are fully granted

from *Chemistry-A European Journal* and *Angewandte Chemie International Edition* for this thesis.

2.1 Introduction

In 1958, Ralph N. Adams developed a carbon paste electrode (CPE) to study the electrochemistry of insoluble compounds.⁶ Carbon paste electrodes were initially made by packing a mixture of graphite, insoluble compounds and organic oil into a hollow teflon tube. This method was developed extensively by electrochemists in the USSR⁷⁻¹¹ as reviewed by Scholz.¹²⁻¹⁶ More recent and comprehensive reviews on the applications and developments of carbon paste electrode were reported by Švancara *et al.*¹⁷⁻²⁰

In the late twentieth century, other electrochemical methods such as abrasive attachment were used for the electrochemical study of insoluble solids.¹² In 1991, a reductive differential pulse voltammogram of α -HgS was reported by Scholz *et al.* with a large reductive peak seen at -1.5V vs SCE;²¹ solid α -HgS was “mechanically” transferred to a paraffin impregnated graphite electrode.³ Generally, the redox products of solid particles are typically water-soluble. Depending on the electrochemical system of the solid of interest, the products may diffuse into the bulk solution or remain on the electrode. Previously, polymer films have been used to immobilise solid particles on electrodes and sample “recuperation” was seen after the electrochemical measurements.²²⁻²⁵

Herein, a new composite containing carbon black, polyvinylidene fluoride (PVDF), N-Methyl-2-pyrrolidone (NMP) and an insoluble solid of interest was dropcasted onto a glassy carbon electrode and subsequently dried to form a carbon/PVDF based composite electrode. The PVDF binds the solid of interest while the carbon black confers electronic conductivity. At the same time, the composite is sufficiently porous for the solid under

Chapter 2: Electrochemistry of Insoluble Particles

study to ‘see’ electrolyte solution. Together, the layers of carbon and PVDF hinder the diffusion and loss of the redox products into the solution, even when products are normally water-soluble. The characteristics of this composite are first compared to other previously developed methodologies using three well-studied water-insoluble organic compounds; namely 9,10-anthraquinone, oil blue N dye and indigo. Having characterised the intrinsic properties of this carbon/PVDF composite, the focus then turns to the electrochemistry of α -HgS. The use of this carbon/PVDF composite reveals a cyclic voltammogram of the reduction of solid α -HgS for the first time and shows the subsequent re-oxidation of sulphide and anodic stripping of metallic mercury. Lastly, the collaborative work using the new composite facilitating an in situ electrochemical X-ray diffraction experiments on solid β -Fe_{1+x}Se particles is highlighted towards the end of this chapter.

2.2 Experimental

2.2.1 Chemicals

All chemicals used were of analytical grade and were purchased from Sigma-Aldrich except carbon black²⁶ (diameter 27 ± 10 nm, Monarch 430, Cabot Performance). The Polyvinylidene fluoride (PVDF), supplied by Sigma-Aldrich, has an average molecular weight of 5.34×10^5 atomic mass units by gel permeation chromatography. These chemicals were used without further purification. The β -Fe_{1+x}Se was synthesised by Dr Rasche from pestle and mortar mixing of iron and selenium in an argon-filled glovebox ($pO_2 / p^0 < 1$ ppm) following by heating under vacuum to 430 °C for a period of two days.⁵ Aqueous solutions were made using ultrapure water (Millipore, resistivity of 18.2 M Ω cm measured at 25°C). Nitrogen gas (99.998%, BOC Gases plc, Guildford UK) was used to de-oxygenate the electrolytic solutions at a sufficient intensity and for a sufficient

period of time to ensure no measurable oxygen signal is observed in the voltammogram except where discussed below.

2.2.2 Carbon/PVDF Composite Modified Electrodes and Electrochemical Equipments

The carbon/PVDF composite contains a mixture of the insoluble material under study, carbon black and PVDF (dissolved in NMP, 25mg/ml) in a weight ratio of 20:60:20 unless otherwise specified. This weight ratio was selected for a balance of obtaining a good electrochemical signal for the solid of interest whilst maintaining electrical contact with the carbon black and enough PVDF to maintain a strong physical binding. The carbon/PVDF composites were stirred overnight, and 2 μ l was dropcasted onto a glassy carbon working electrode ($r_e = 1.50$ mm, CH Instruments, TX, USA). The modified working electrode was subsequently dried overnight at 70° C to evaporate off the NMP solvent.

Either a saturated mercury sulphate (MSE), a saturated calomel electrode, SCE, (SCE, BAS Inc., Japan) or a leakless miniature Ag/AgCl (World Precision Instruments, Sarasota, USA) reference electrode was used. The three-electrode cell configuration was completed using a carbon rod counter electrode. The electrochemical experiments were conducted with a computer-controlled Autolab potentiostat 30 (Metrohm Autolab B.V., Utecht, The Netherlands) using NOVA 2.0 with the “alpha value” set to 0.3. The latter controls the point of current sampling in the staircase ramp.²⁷ The carbon/PVDF composite modified GC electrode was polished after each experiment with 3, 1, 0.1 μ m diamond spray (Kemet, UK) in descending order of size. The diamond spray residue was then removed from the electrode surface by rinsing with excess ultrapure water and subsequently dried under a nitrogen flow.

2.2.3 In situ Electrochemical X-ray Diffraction Experiment

The cell facilitating the electrochemical X-ray diffraction experiments was designed by Dr Kleiner (Diamond Light Source) together with Dr Rasche. An illustration of the cell and the experimental cell set up at beamline I11 is shown in Figure 2.1. The cell body is made of Teflon. The working electrode is a carbon/PVDF composite modified 0.5mm thin glassy carbon disc (Hochtemperatur-Werkstoffe GmbH, Germany) which seals with a rubber O-ring against the inner of the cell and is contacted from the outside by a metal frame and a spring. The counter electrode is a graphite rod and the reference electrode is an Ag/AgCl reference electrode, both of which has a diameter of 2mm and are sealed with an O-ring against the inner of the cell and can be contacted by a crocodile clip. The cell was assembled, filled and sealed inside an argon-filled glove box prior to the in-situ electrochemical X-ray diffraction experiments.

In situ electrochemical X-ray diffraction experiments were performed with a wavelength of $\lambda = 0.494 \text{ \AA}$. The temperature of the cell during the experiment was maintained at 65 °C by temperature sensor-controlled heat gun. A Mythen2 detector (position sensitive detector) with an exposure time of 20 s was used for continuous measurements during the experiment. Phases were first identified with WinXPow²⁸ and Rietveld refinement was performed with TOPAS Academic Version 5.²⁹

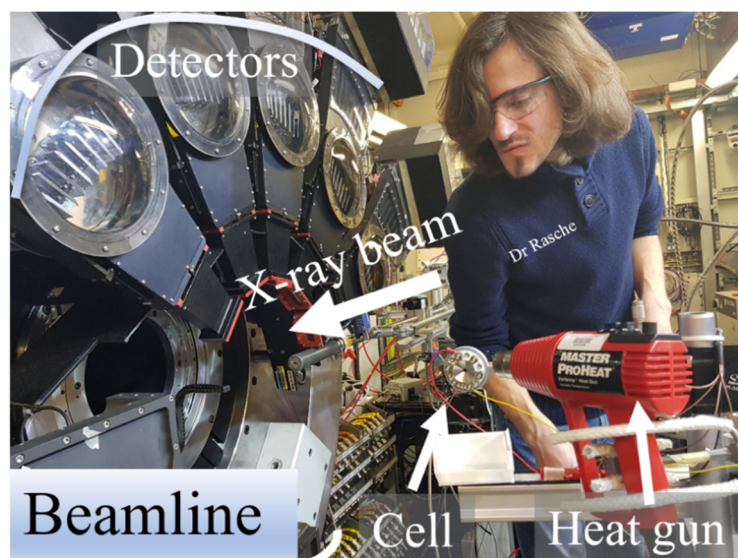
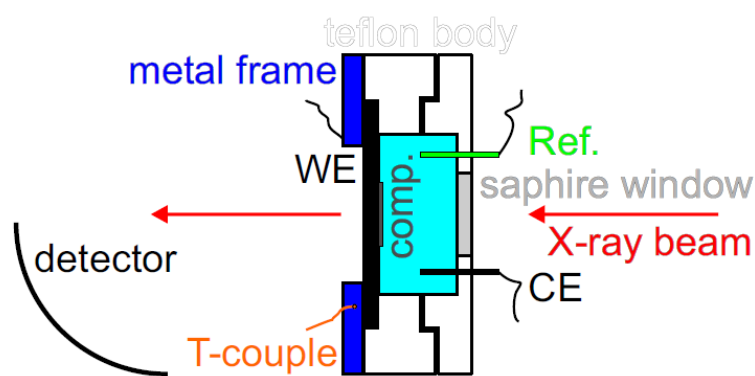


Figure 2.1. Top: a sketch of the in-situ electrochemical X-ray diffraction cell. Middle: electrochemical cell mounted in the experimental hutch. The temperature sensor controlled heat gun can be seen on the right. The potentiostat is out-of-view. Bottom: picture of the control cabin, shielded from radiation. Photo credit: Minjun Yang (me).

2.2.4 Buffer Solutions

Buffer solutions are used in two different sets of electrochemical experiments in this chapter - indigo (Section 2.3.1) and β -Fe_{1+x}Se (Section 2.3.3). The pH measurement was performed with a pH 213 microprocessor pH meter (HANNA Instruments, Leighton Buzzard, UK) and a pH electrode (HI 1131, HANNA Instruments), which was calibrated before use.

Indigo

The pH buffer solutions used contained a diversity of 0.1M KNO₃ based solutions, as shown in Table 2.1. The precise pH was adjusted to the indicated value using small amounts of 1M HCl/NaOH.

Table 2.1: Composition of the pH buffered solutions used in the indigo electrochemical experiments in 0.1M KNO₃ electrolyte (Section 2.3.1). The numbers in the table are the volume of each constituent used to make 100 ml of the final buffer solution of the specified pH.

	Solution composition in 0.1M KNO ₃ / mL					
pH	0.1M citric acid	0.1M potassium phosphate dibasic	0.1M potassium phosphate monobasic	0.1M sodium carbonate	0.1M sodium bicarbonate solution	0.1M sodium hydroxide
5.0	24.3	51.4				
7.0		61.0	39.0			
9.0				4.0	46.0	
11.0				42.5	7.5	
13.0						100.0

β -Fe_{1+x}Se

Citric buffer was prepared from 0.16M sodium citrate tribasic and 0.02M citric acid followed by an adjustment of the pH to 7.2 by adding solid KOH. This buffer solution was used for the in situ electrochemical X-ray diffraction experiment in (Section 2.3.3). The solution was degassed for 1 h by bubbling with nitrogen and transferred into an

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argon-filled glove box, where the solution was degassed by bubbling with argon for another 30 min.

2.2.5 Scanning Electron Microscopy

Scanning electron microscope images were taken on a Zeiss Sigma 300 FEG-SEM at an accelerating voltage of 10.0 KV, 15 μm aperture and 3610X magnification. The carbon/PVDF composites were stirred overnight. A carbon fibre stub was polished with aqueous slurries of 1, 0.3 and 0.05 μm alumina in decreasing order of size, followed by 30 minutes of sonication and immersed in aqua regia overnight before rinse and dry. Two μL of the carbon/PVDF composite was then dropcasted onto the carbon fibre stub and dried overnight at 70 $^{\circ}\text{C}$.

2.3 Results and Discussions

The electrochemical behaviour of the carbon/PVDF composite is first studied with three well-known water insoluble organic compounds: namely 9,10-anthraquinone, oil blue N dye and indigo. The mechanistic pathways and electrochemical reactions of those organic compounds are well known in the literature but are studied herein to characterise the behaviour of the composite so as to validate the methodology. Subsequent attention turns to apply the carbon/PVDF composite to facilitate the electrochemistry of α -HgS and the collaborative work on a superconductor β -Fe_{1+x}Se.

2.3.1 Characterisation of The Carbon-composite Material

9,10-anthraquinone

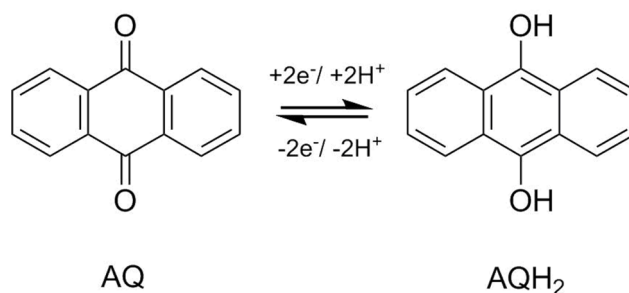


Figure 2.2. Chemical structure of 9,10-anthraquinone (AQ) and the electrochemical reactions.

The reduction process of quinone functional groups are generally two-electron transfer in aqueous media to form, depending on pH, the corresponding hydroquinone or quinone dianion.^{30, 31} In organic aprotic solvents, 9,10-anthraquinone (AQ) and similar derivatives undergoes two successive one-electron reductions to form the corresponding semiquinone AQ^{•-} and the dianion AQ²⁻; two separate waves can be seen on the reductive sweep.^{32, 33} Since AQ is insoluble in water, electrochemical studies have usually been conducted with either ‘surface-tethered’ AQ or similar derivatives that are water-soluble.³⁴ In acidic buffered aqueous solutions, the overall reduction pathway is a stepwise two-electron and two-proton via a “scheme-of-squares”³⁵ to form the

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corresponding hydroquinone.^{34, 36} In alkaline buffered aqueous solutions, the reduction process is two stepwise electron transfer reactions to form the corresponding quinone dianion.³⁴ Note, only one apparent wave was seen on the reduction in buffered aqueous solutions across all pH values.³⁷ This is ascribed to the hydrogen bonding stabilisation leading to “potential inversion” at the quinone/semiquinone and semiquinone/hydroquinone couple.³⁸⁻⁴⁰

The cyclic voltammogram recorded on an AQ carbon/PVDF composite working electrode in pH 13 NaOH buffered solution at a scan rate of 30mVs^{-1} is depicted in Figure 2.3. On the first cycle, a high negative over-potential was required to initiate the redox chemistry of solid AQ. On subsequent cycles, redox signals corresponding to the two-electron transfer reaction were seen with a formal potential around -1.19 V vs MSE .⁴¹ This initiation process in the first cycle is familiar as a “break-in” reaction in solid-state electrochemistry.^{42, 43} In solution phase electrochemistry, charge neutrality can be rapidly achieved by diffusion of nearby electrolyte upon electron transfer. In solid-state electrochemistry, however, the electrolyte cannot diffuse freely into the solid crystalline or amorphous structure and over-potential is required to ‘break’ the structural integrity. The break-in reaction was only observed on the first cycle. It is likely that upon the initial reduction, the formed AQ^{2-} species diffuses within the composite and on the reverse sweep, is oxidised to form smaller sized AQ crystals. The peak current decreases upon consecutive cycles. This indicates some loss of material from the electrode during each cycle. This is likely due to the escape of the water-soluble product AQ^{2-} into the bulk solution by diffusion. Note, a large IR drop was observed in the cyclic voltammogram of AQ, which results in the large magnitude of the peak to peak separation.

For the voltammetry of non-diffusing species, the peak current is expected to scale linearly with scan rate with an intercept at zero.^{1, 44} In the case of AQ carbon/PVDF

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composite, the break-in reaction takes place on the first cycle and therefore the relationship of peak current and scan rate were investigated on the 2nd cycle, shown in Figure 2.4. The inlay of Figure 2.4 shows a plot of peak current against scan rate. As can be seen, the relationship of peak current and scan rate deviates from linearity at high scan rates. This can be in part ascribed to the reduced time available for the break-in reaction to occur entirely on the first cycle. Therefore, less ‘activated’ AQ is available for reduction on the second cycle which leads to a decrease in peak current as the scan rate increases.

In comparison to the voltammogram of solid-phase AQ reported by Kuwana and French using a CPE,⁴¹ the break-in reaction was observed using the carbon/PVDF composite but not with a CPE where the AQ is likely dissolved in the oil used as the binder. The carbon/PVDF composite is therefore a complementary approach to the CPE for a thorough electrochemical analysis of solids such as AQ.

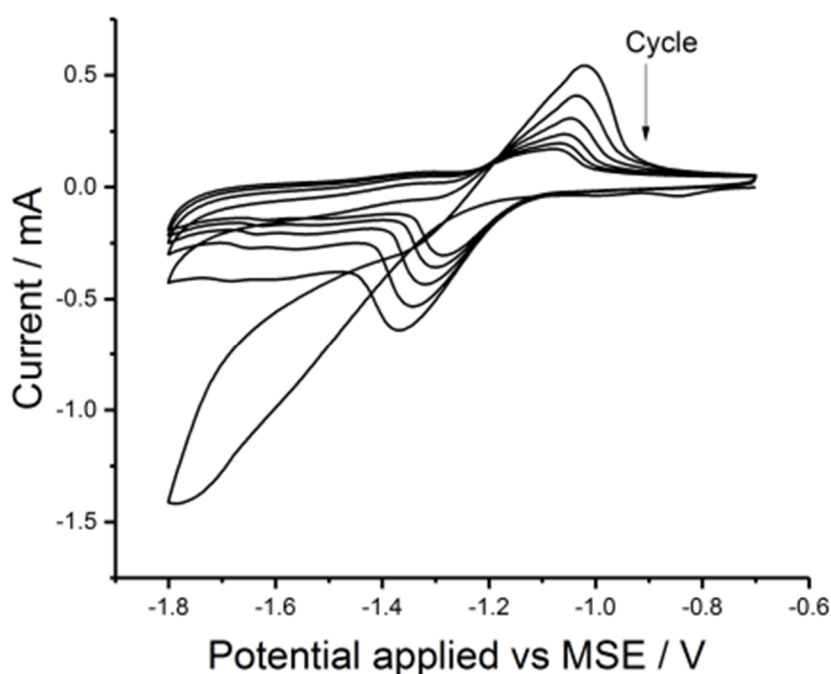


Figure 2.3. Cyclic voltammogram recorded on a 9,10-anthraquinone carbon/PVDF composite modified electrode. The first 6 cycles are shown and recorded consecutively in a degassed solution containing 0.10 M KNO₃ electrolyte buffered at pH 13 with NaOH at a scan rate of 30 mV s⁻¹. The composite contains a mixture of 9,10-anthraquinone, carbon black and PVDF in a weight ratio of 20:60:20.

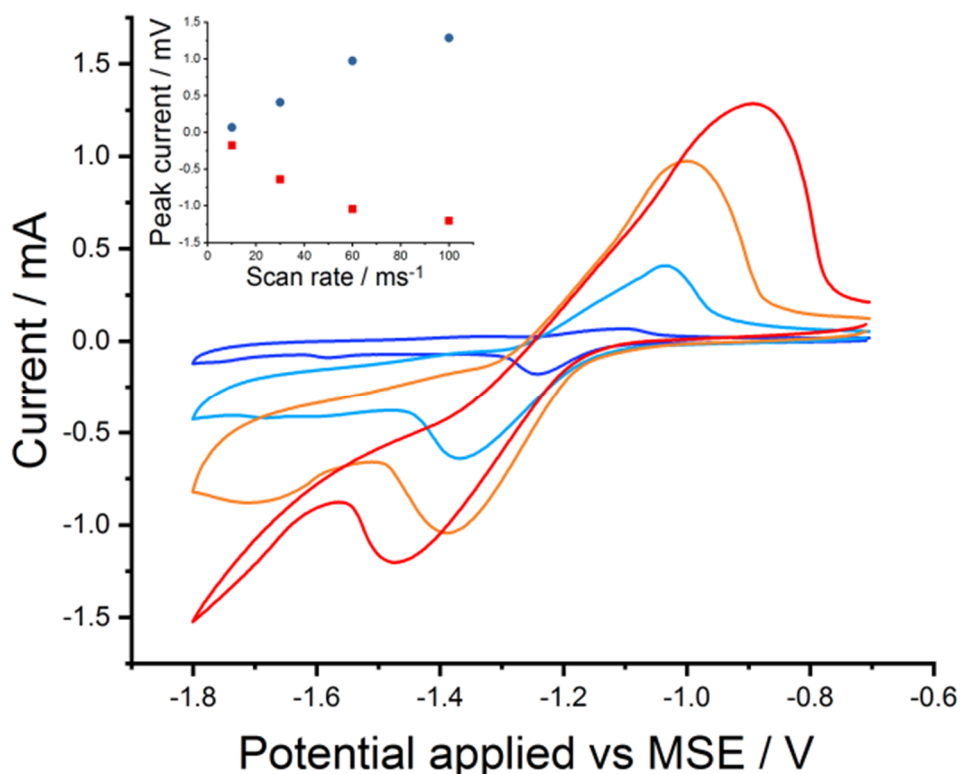


Figure 2.4. The 2nd cycle recorded on a 9,10-anthraquinone carbon/PVDF composite modified electrode at different scan rates. The solution is degassed and contains 0.10 M KNO₃ electrolyte with NaOH buffering at a pH of 13. The scan rates of 10, 30, 60 and 100 mV s⁻¹ are displayed with dark blue, blue, orange and red line. Inlay, peak current versus scan rate. The composite contains a mixture of 9,10-anthraquinone, carbon black and PVDF in a weight ratio of 20:60:20.

The key behaviour of the composite can be deduced from the AQ carbon/PVDF composite; the molecules formed from the redox reaction, such as AQ²⁻ or AQH₂, can diffuse out of the composite but only slowly in the voltammetric time scale. This was evidenced by the relatively weak decrease in peak current upon consecutive cycles. This observation is in contrast to “abrasive voltammetry”. The focus in the next section turns to the electrochemistry of oil blue N dye in carbon/PVDF composite.

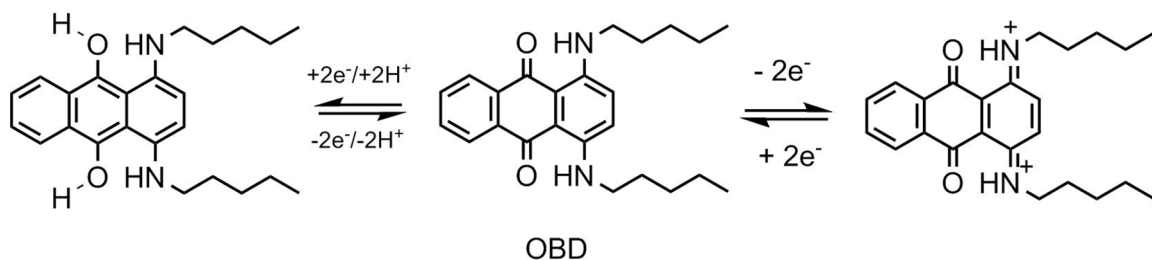
Oil blue N dye

Figure 2.5. Chemical structure of oil blue N dye (OBD) and the electrochemical reactions.

The redox chemistry of oil blue N dye (OBD, Figure 2.5) is known to be bifunctional, such that both reduction and oxidation can occur.⁴⁵ The processes in water are the two-electron reduction of the quinone function group and the two-electron oxidation on the phenylenediamine group, as reported previously.⁴⁵ The cyclic voltammograms obtained for the reduction of oil blue N dye carbon/PVDF composite in aqueous solution, at a scan rate of 10 mVs⁻¹, are shown in Figure 2.6. Reductive signals were observed at potentials of -0.97 V and -1.11 V vs MSE respectively, the latter is attributed to the two-electron reduction of the quinone group.^{34, 46, 47} The reduction peak at -0.97 V vs MSE is ascribed to the reduction of oxygen, as it is also observed in the control experiment measured using a ‘blank’ carbon/PVDF composite unloaded with OBD. Note that the oxygen is present in the composite despite degassing the solution to the extent that no voltammetric signal would be seen on a non-porous electrode.

The oxidation of OBD in the carbon/PVDF composite is shown in the inlay of Figure 2.6. The first cycle (orange line) shows little redox activity in comparison to the second cycle (red line), likely due to the occurrence of a “break-in” reaction as observed with the reduction of 9,10-anthraquinone. The second cycle of the oxidation of OBD shows oxidative peaks at +0.12 and +0.40 V vs MSE, the peak potentials are in agreement with the previous report by direct dropcast of OBD on a glassy carbon electrode.⁴⁵ A back wave can be seen on the oxidation of OBD with the use of carbon/PVDF composite but

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not when directly dropcast onto an electrode surface.⁴⁵ The oxidised species of OBD will likely be water-soluble as it bears a positive charge. Therefore, it is expected to completely diffuse and escape into the bulk solution from a direct dropcast onto an electrode surface.⁴⁵ By using the carbon/PVDF composite, the diffusion oxidised OBD species is hindered by the layers of carbon held together using PVDF and hence a back wave is seen on the reverse sweep.

The redox potentials of OBD obtained using the carbon/PVDF composite are consistent with the direct OBD dropcast measurement. Moreover, since the formed products do not completely diffuse out of the carbon/PVDF composite layers within the experimental time scale, additional electrochemical information can be obtained for the redox couple. The presence of oxygen in the carbon/PVDF composite may distort the voltammetric signal of other solids of interest; this can be overcome by increasing the weight ratio of the solid of interest or preparing the carbon/PVDF composite electrode and conducting the experiment inside a glove box, under a nitrogen atmosphere. The next section will discuss the behaviour of indigo containing carbon/PVDF composite in pH buffered solutions.

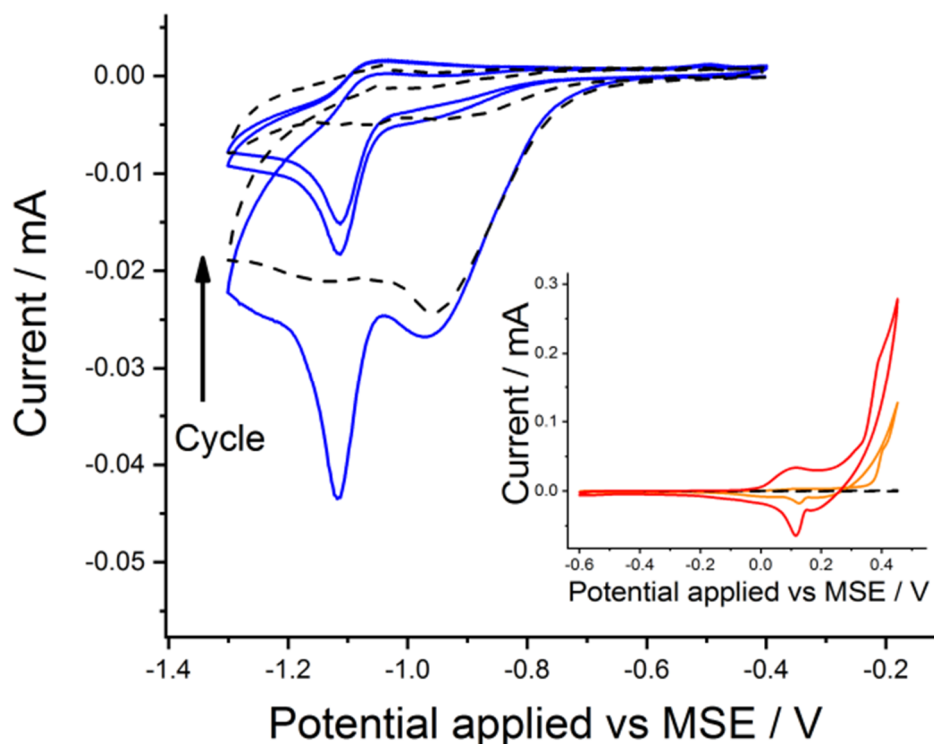


Figure 2.6. Cyclic voltammograms of an oil blue N dye carbon/PVDF composite modified electrode. The voltammogram swept reductively from -0.40 V and returns at -1.30 V vs MSE. Inlay, voltammogram swept positively from -0.60 V to $+0.45\text{ V}$ vs MSE at a scan rate of 10 mVs^{-1} . Solid lines - composite of oil blue N dye, carbon black and PVDF in a weight ratio of 20:60:20. Dotted line – control experiment measured on a blank carbon/PVDF composite (carbon black and PVDF, weight ratio of 60:20) modified electrode. The measurements were conducted in a degassed solution contains 0.1M KNO_3 electrolyte and pH 7.0 PBS buffer.

Indigo

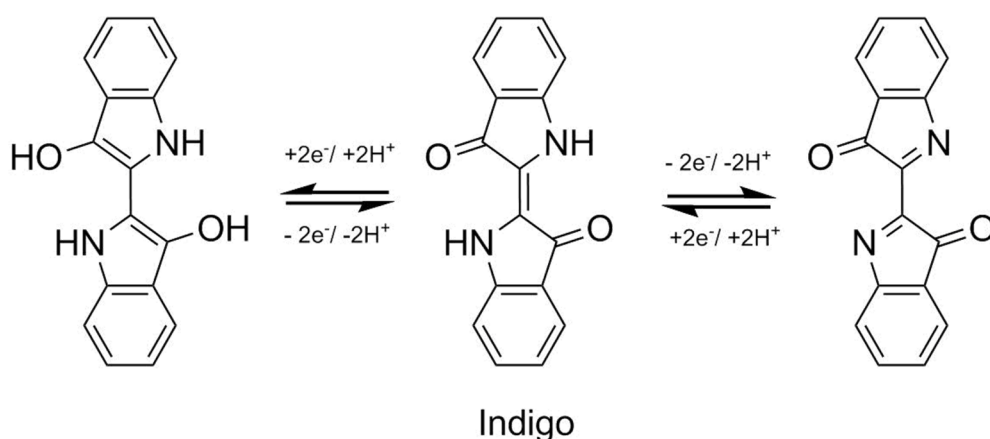


Figure 2.7. Chemical structure of indigo and the electrochemical reactions in the presence of protons.

The natural occurring dye indigo is used for textile dyeing, most commonly used for denim cloth, due to its vibrancy and the rare distinctive deep blue hue.⁴⁸ To meet the

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demand of the fashion in denim, 50,000 tonnes of indigo have been produced synthetically per year since 2011.^{49, 50} As indigo is water-insoluble, it cannot penetrate into or bind to cloth fibre. To apply the dye, the dye industry reductively converts the insoluble indigo to the water-soluble leuco-indigo form via two-electron reduction in a batch process. The leuco-indigo is then oxidised by atmospheric oxygen to return the insoluble indigo, which adsorbs to cloth fibre. Unlike other synthetic blue dyes, indigo adsorbs to the cloth fibre instead of forming covalent bonds with it. The adsorbed indigo is robust to harsh detergents used for laundering, yet it wears out with persistence abrasion to reveal the white fibre core, which results in a desired worn-out look for a personalised jean and renders it irreplaceable by other synthetic blue dyes.⁵¹

Bond *et al.* reported the electrochemistry of solid-state indigo by “mechanically attachment” to a basal plane pyrolytic graphite electrode (BPPG), pH buffered at a range of 5.0 to 13.0.⁴³ In our work, a series of cyclic voltammograms were recorded using an indigo carbon/PVDF composite buffered at the corresponding pH values, shown in Figure 2.8. The voltammograms start at -0.4 V and were swept negatively at scan rates of 10mVs⁻¹ to -2.0V vs MSE. A large reductive wave was seen at -1.5V vs MSE, labelled process 1. On the reverse scan, two reversible redox processes, labelled process 2 and 3 are seen with formal potentials of -0.72 V and +0.07 V vs MSE at pH 5.0 respectively. Process 1 was only seen on the first cycle and ascribed as the “break-in” reaction.⁴³ Both of the midpoint potentials for process 2 and 3 were found to vary with pH by -57 ± 3.0 mV and -63.4 ± 1.4 mV per pH unit respectively, in agreement with the results reported by Bond et.al.⁴³ The voltammograms obtained using the carbon/PVDF composite was mostly identical to that mechanically attached to BPPG, except that additional waves was seen at pH 9.0 and 13.0. At a higher scan rate of 30mVs⁻¹, multiple peaks appear with each process and have no correlation to the buffered pH. This phenomenon was ascribed

to the poor pH buffering inside the composite. The diffusion of buffering species into the composite is slow, which is analogous to the observation of back wave for the oxidation of OBD. The slow buffering effect is similar to that observed with a partially buffered solution, where the pH at the electrochemical interface alters as the finite pH buffering species were consumed.³¹ Therefore, caution is needed in interpreting voltammograms obtained with the carbon/PVDF composite when the electron transfer is accompany by the uptake of protons or reaction with hydroxide ions.

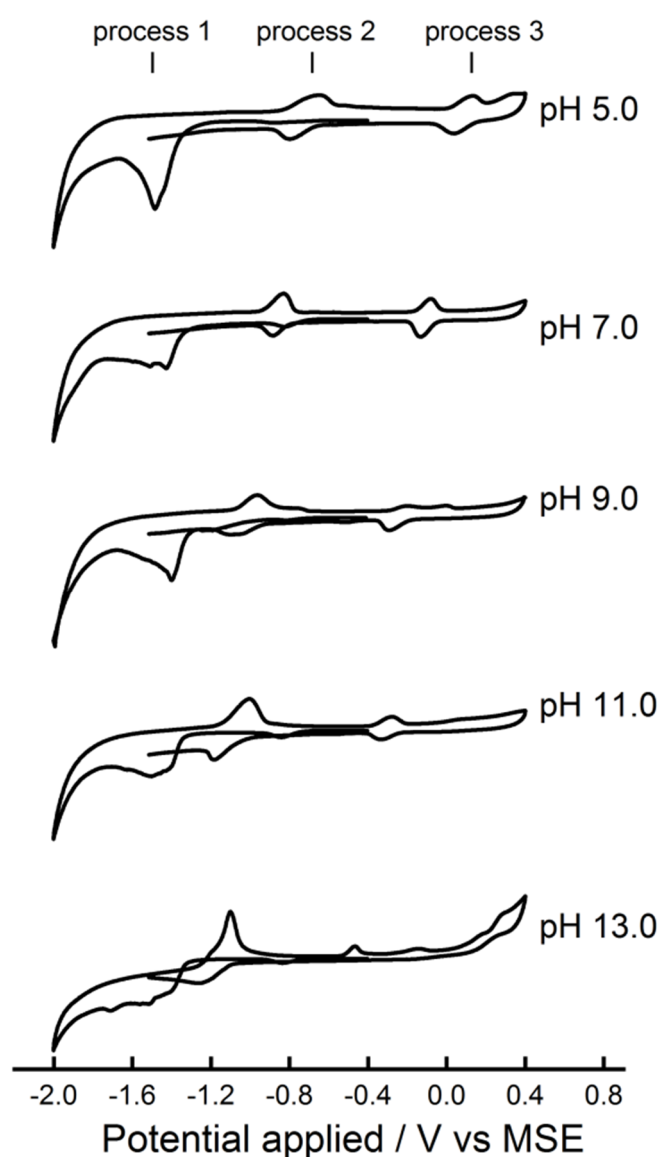


Figure 2.8. Cyclic voltammograms recorded on indigo carbon/PVDF composite modified electrodes immersed in degassed 0.1M KNO_3 and pH buffered solution. The potential was first swept negatively from -0.40 V to -2.00 V, then reverse direction and swept positively to +0.40 V before returning to -1.50 V vs MSE. The composite contains a mixture of indigo, carbon black and PVDF in a weight ratio of 20:60:20.

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In summary, the carbon/PVDF composite electrode has demonstrated its ability to facilitate the electrochemistry of various solid particles. By imbedding the solid materials in the layers of carbon/PVDF, the diffusion of the formed charged species into the bulk solution is hindered, and information on the product can be obtained during the return sweep. It can, however, lead to a complicated voltammogram in pH buffered solutions with electrochemical processes that involve the uptake of protons or hydroxide ions. This is due to the hindered diffusion of species from the bulk solution into the carbon/PVDF composite, which results in a 'slow' buffering effect. Moreover, atmospheric oxygen was found adsorbed in the composite, the signals can be distinguished from the solid of interest by varying the weight ratios of the solid or to fabricate the carbon/PVDF electrode under nitrogen atmosphere.

Having understood the electrochemical behaviours of the carbon/PVDF composite the next section turns to mercury sulphide. First, the historical use of this naturally forming mercury mineral is discussed.

2.3.2 Mercury Sulphide (α -HgS)

Natural occurring forms of mercury are found commonly as minerals of which the most important are red cinnabar and black metacinnabar. The red cinnabar, α -HgS, is more abundant than the black metacinnabar (β -HgS) and it is commonly found near volcanos and has been used as pigments and in cosmetics since ancient times. Metallic mercury can be extracted by heating solid α -HgS with a flux of air followed by vapour condensation. Mercury and mercury salts are commonly known for their high toxicity.⁵²⁻

⁵⁴ Disposal of untreated mercury wastewaters into the aquatic environment forms methylmercury by bacteria methylation,⁵⁵ a neurotoxin responsible for Minamata disease.^{56, 57} Despite the notorious toxicity of mercury compounds, some traditional Chinese medicines retain the use of α -HgS as part of their recipes. A commercial Chinese

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medicine, An-Gong-Niu-Huang Wan, is currently banned for sales in USA and Japan due to the cinnabar and realgar (β -As₄S₄) content.^{58, 59} At room temperature, α -HgS is thermodynamically more stable than β -HgS.⁶⁰⁻⁶² However, it is β -HgS that usually precipitates from the solution phase.⁶²⁻⁶⁵ The transition temperature of cinnabar-metacinnabar for stoichiometric mercury sulphide at 1 atmospheric pressure is reported to be 643K.^{61, 63, 66} Both α -HgS and β -HgS are extremely insoluble in aqueous solution, the logarithm of the corresponding solubility products were reported around -53 and -52 at 298K respectively.^{62, 67-74} Perhaps due to its insolubility, the toxicity of mercury sulphides are relatively low compared to other forms of mercury.⁵⁸

The electrochemical analyses of solid α -HgS were facilitated by using α -HgS carbon/PVDF composite modified GC electrodes, where the composite layer is typically 100-1000 μ m in thickness. The inlay a) and b) of Figure 2.9 shows the surface topography imaged with a scanning electron microscope using backscattering (BSE) and secondary electron (SE) detectors respectively. The secondary electron image shows the presence of solid α -HgS particles, of sub-microns in size, on the surface of the carbon/PVDF composite. In contrast to the backscattered electron images, it reveals that the majority of the solid α -HgS are imbedded in the carbon/PVDF composite.

Figure 2.10 shows a series of cyclic voltammograms recorded on α -HgS carbon/PVDF composite electrodes, with reverse potentials ranging from -1.60V to -2.00V vs MSE (10 mVs⁻¹). On the forward sweep, no apparent peak was seen for the reduction of α -HgS solid. On the backward sweep, however, two oxidative signals were seen at potential of -0.49V and +0.24V vs MSE, and the magnitude of those peaks increases with higher negative return potential. At these high negative potential, the solid α -HgS is thought to reduce simultaneously with the occurrence of hydrogen evolution reactions (HER) at the electrode interface. The reduction of solid α -HgS likely forms metallic mercury and S²⁻,

but the reduction peak was not seen for α -HgS as the current was dominated by the HER. Since the standard reduction potential of Hg^{2+}/Hg is +0.85V vs NHE (+0.21 vs MSE),⁷⁵ the oxidative peak at +0.24V vs MSE is ascribed to the anodic stripping of metallic mercury and -0.49V vs MSE is the oxidation of sulphides within the composite. The inlay b) in Figure 2.10 shows a plot of the mercury stripping charge versus return potential and a sharp gradient can be seen around -1.8 to -1.9 V. The stripping charge of mercury is directly correlated to the amount α -HgS reduced; the reduction peak potential of α -HgS is therefore within the range of -1.8 to -1.9 V vs MSE. Furthermore, inlay a) in Figure 2.10 shows a square wave voltammogram measured on the α -HgS carbon/PVDF composite electrode with a reductive peak appearing at a potential of -1.82V vs MSE, which is not dissimilar to the differential wave voltammogram reported by Scholz *et al.* using a paraffin impregnated graphite electrode.²¹ Moreover, a number of reductive spikes were seen after the return potential of -1.95V and -2.00V vs MSE; this can be tentatively ascribed to the reduction of large HgS particles as a result of an applied over-potential.

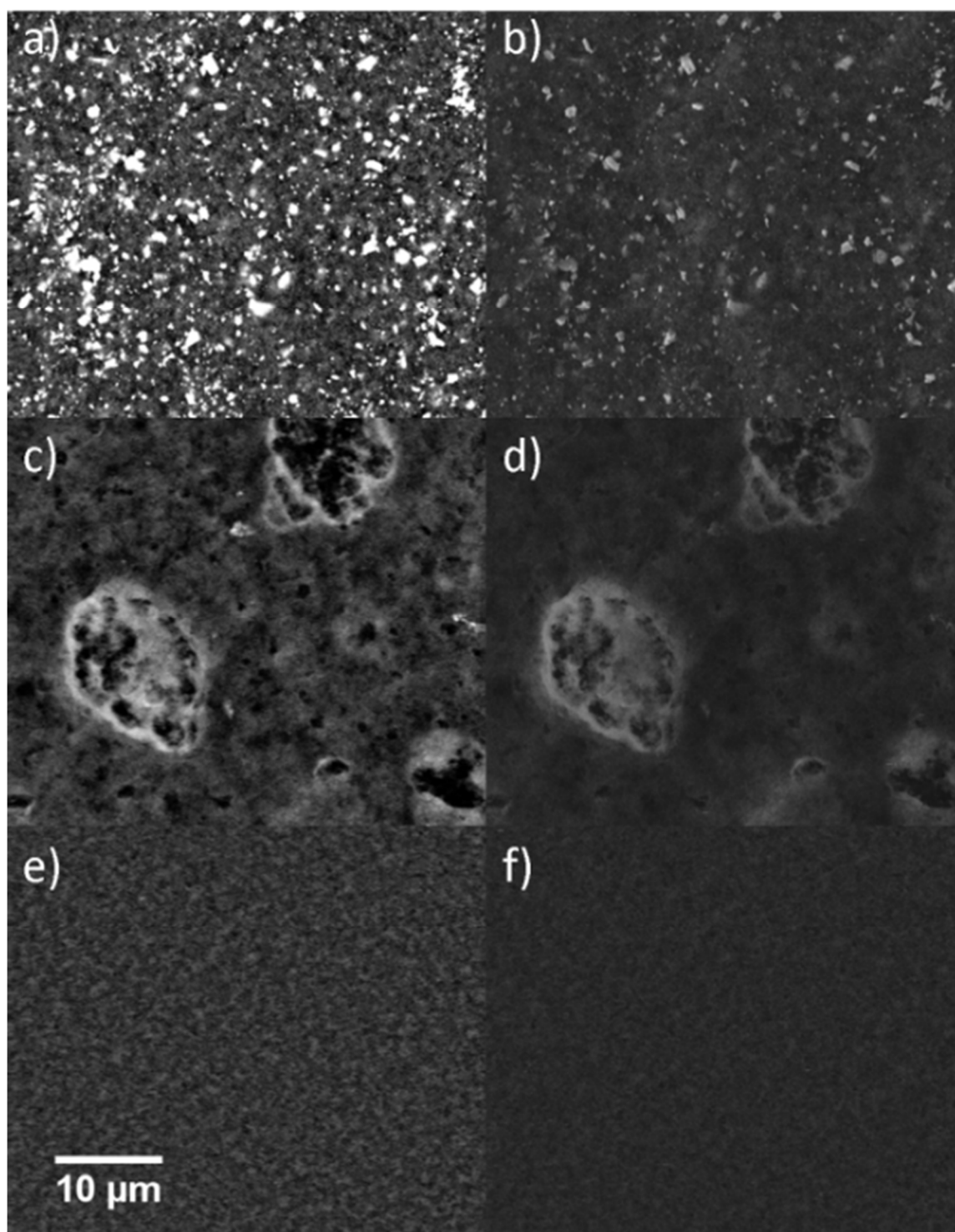


Figure 2.9. Scanning electron microscope images of various carbon/PVDF composites using the backscattering electron detector (a, c and e) and secondary electron detector (b, d and f). The brightness and contrast settings were identical across all the backscattering electron images. The α -HgS carbon/PVDF composite - inlay a) and b); sulphur carbon/PVDF composite - inlay c) and d); the weight ratio of the composite is 20:60:20 (α -HgS/S: carbon black: PVDF). Blank carbon/PVDF composite – inlay e) and f), the weight ratio of carbon black to PVDF is 60:20.

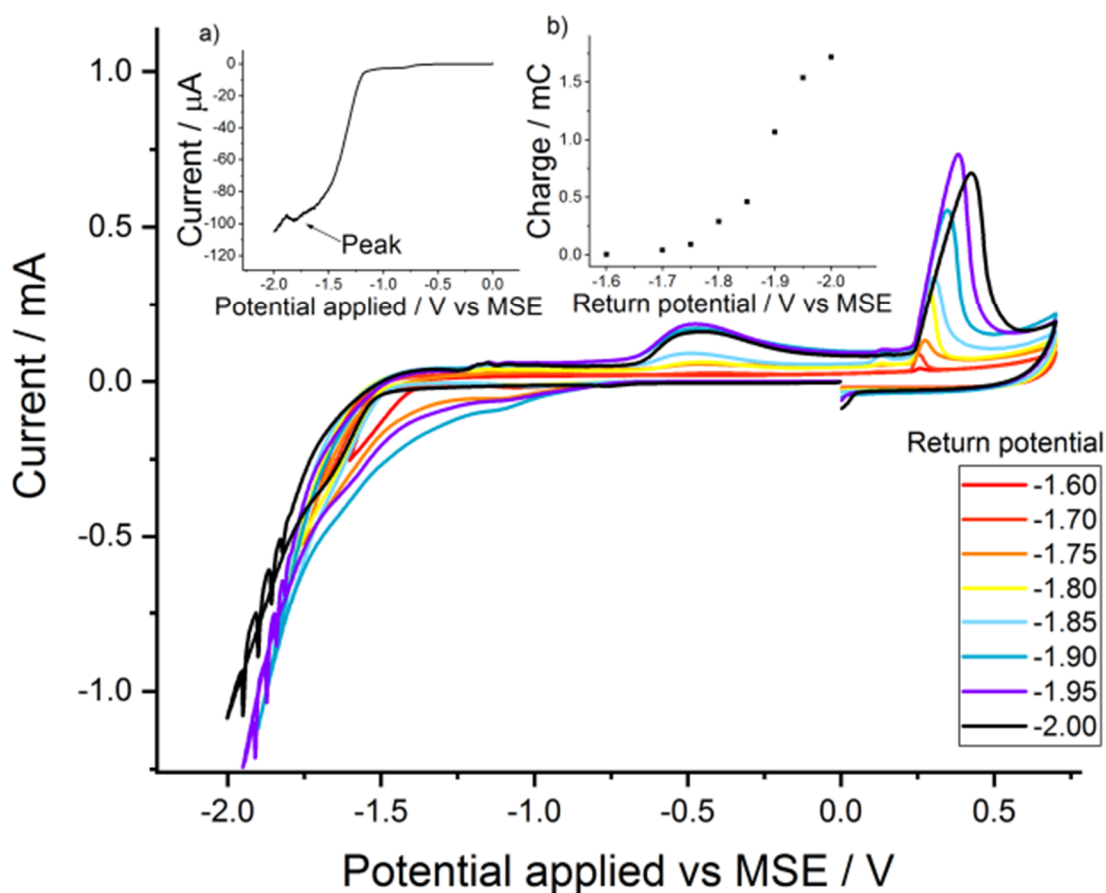


Figure 2.10. Cyclic voltammograms of glassy carbon electrode modified by dropcasting a composite of α -HgS, carbon black and PVDF, recorded in degassed pH buffered solution of 0.10 M KNO_3 at a scan rate of 10 mVs^{-1} . Inlay, a) reductive square wave voltammogram of the α -HgS composite modified GC electrode with experimental parameters of 2 mV step potential, modulation amplitude of 10 mV and frequency of 10 Hz. Inlay, b) plot of charge against the return potential for the oxidative peak at +0.24V vs MSE.

The SEM images of the blank carbon/PVDF composite are shown in the inlays e) and f) of Figure 2.9. The voltammogram of a blank carbon/PVDF composite electrode immersed in a 1.0 mM Hg^{2+} solution is shown in Figure 2.11. The voltammogram swept positively from -1.80 V and an oxidative signal was seen at +0.15V vs MSE. During the forward sweep, mercury deposits on the blank carbon/PVDF composite via two-electron reduction of Hg^{2+} , the oxidation signal at +0.15V vs MSE is therefore the anodic stripping of metallic mercury to reform Hg^{2+} . Interestingly, the stripping potential of mercury recorded on a blank carbon/PVDF composite, +0.15V, is slight lower than that observed with the α -HgS carbon/PVDF composite, +0.24V. This discrepancy can be ascribed to

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the difference in local chemical environment of the mercury. On the oxidative sweep after the reduction of α -HgS composite, sulphides were presumed to oxidise to form sulphur prior to the anodic stripping of mercury. Possibly it is an interaction^{76, 77} between sulphur and mercury that causes slightly higher mercury stripping potential in comparison to that seen in the absence of sulphur. Furthermore, a small amount of sulphur was added into the carbon/PVDF composite to form a sulphur-carbon-PVDF composite with a weight ratio of 3:60:20. The inlay c) and e) of Figure 2.9 shows the backscattering and secondary electron SEM images of the sulphur-carbon-PVDF composite. The cyclic voltammogram measured with this sulphur-carbon-PVDF composite immersed in a 1.0 mM Hg^{2+} solution is shown in Figure 2.12. Two anodic mercury stripping signals can be seen at a potential of +0.11 V and +0.22 V vs MSE. It is evident that, in the limiting sulphur environment, the first oxidation peak at +0.11 V is the stripping of mercury in a chemical environment *without* sulphur and the second at +0.22 V is that *in the presence* of sulphur environment. Thus, it can be concluded that the anodic stripping potential of mercury shifts positively in the presence of a local sulphur-rich environment.

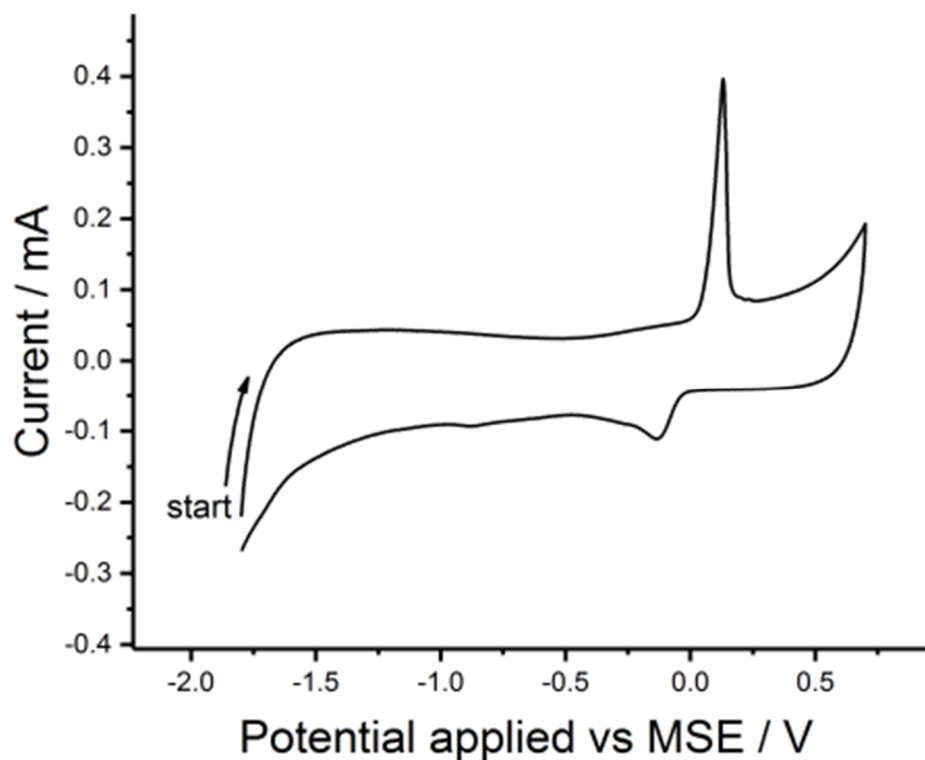


Figure 2.11. Second cycle of the cyclic voltammogram measured with a carbon/PVDF composite modified GC electrode, at a scan rate of 50 mVs^{-1} in degassed aqueous solution containing 1.0 mM HgNO_3 and 0.10 M KNO_3 . The weight ratio of carbon black to PVDF is 60:20.

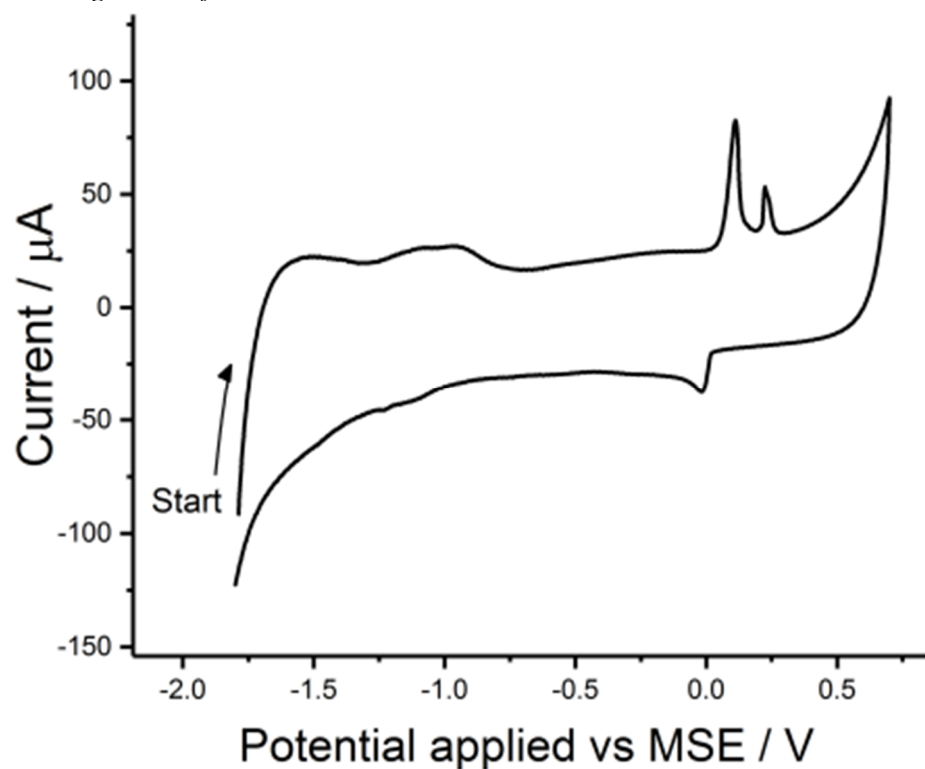


Figure 2.12. Second cycle of the cyclic voltammogram measured with a sulphur carbon/PVDF composite modified GC electrode, at a scan rate of 50 mVs^{-1} in degassed aqueous solution containing 1.0 mM HgNO_3 and 0.10 M KNO_3 . The weight ratio of sulphur, carbon black and PVDF in the composite is 3:60:20.

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Figure 2.13 shows a series of voltammograms recorded on carbon/PVDF composites containing different ratios of sulphur and α -HgS. The oxidation peak potential of sulphide in the absence of α -HgS occurs at -0.75V vs MSE. As the ratio of sulphur to mercury sulphide decreases, the oxidation peak potential of sulphide ions shifts positively, to a potential of -0.49V vs MSE with carbon/PVDF composite containing only HgS. The shift in the sulphide oxidation potential is analogous to that seen with mercury described above, i.e. the oxidation peak potential of sulphide ions shift positively in the presence of a local mercury-rich environment and vice versa.

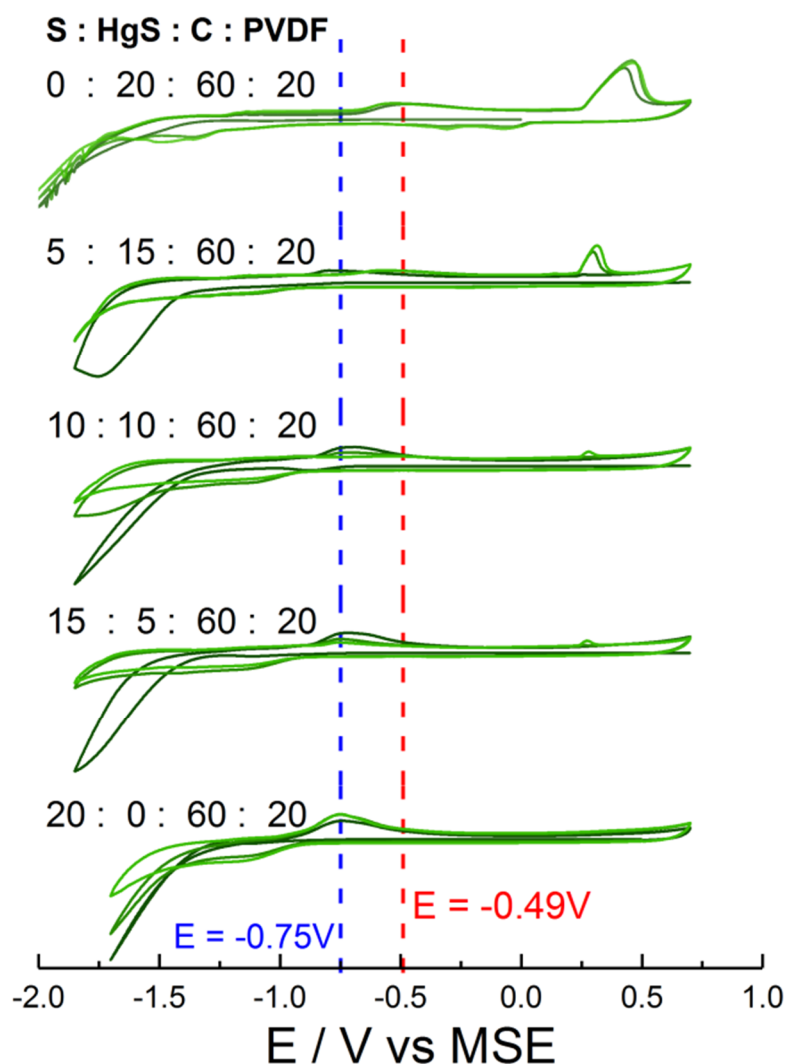


Figure 2.13. Cyclic voltammograms of carbon/PVDF composite containing a different ratio of HgS and S, 3 consecutive cycles were recorded in degassed 0.1M KNO_3 . The cycles 1 to 3 were displayed in colours from dark to light green, respectively.

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To summarise, the cyclic voltammetry of α -HgS is shown and characterised for the first time. Using the carbon/PVDF composite, the reduction peak potential of α -HgS in the square wave voltammetry experiment was found at -1.82V vs MSE and the subsequent oxidation of sulphide and metallic mercury occurred at potentials of -0.49V and +0.24V vs MSE respectively, both shifted slightly positively compared to that measured in isolation using a blank carbon/PVDF composite. This shift in potential is ascribed to the interaction of mercury with the local sulphide environment.

2.3.3 β -Fe_{1+x}Se

This section reports the collaborative carbon/PVDF composite project with Dr Bertold Rasche leading to the publication in *Angew. Chem.*⁵ It begins with a short background introduction to the aqueous insoluble solid of interest, the iron-based superconductor β -Fe_{1+x}Se, follow by results and conclusion from the key in situ electrochemical X-ray diffraction (XRD) experiments performed at the Diamond Light Source.

The data acquisition herein was collected by Dr Rasche, Dr Cooper (staff scientist at ISIS Neutron and Muon Source) and myself at the Diamond Light Source, Oxford. The post-experiment data analysis was realised by Dr Rasche apart from input from Dr Enno Kätelhön (RGC group) with Python scripting. Dr Murray, Dr Day and Dr Kleiner offered their generous technical support at the beamline I-11.

In situ Electrochemical X-ray Diffraction Experiment

Iron Selenide is the simplest iron-based superconductors consisting of Fe²⁺ cations and Se²⁻ anions. Recent interest in iron selenide has grown since 2014 where a thin film of FeSe grown on SrTiO₃ has been reported as a high-temperature superconductor with the critical temperature (T_c) > 100K.⁷⁸ Despite the seemingly ‘simple’ 1:1 stoichiometry of iron selenide, a close look at the phase diagram (Figure 2.14) reveals several non-stoichiometric phases of iron selenide between 49% ≤ Se ≤ 53%. This includes α - and β -

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phases at temperatures below 350 °C and above which forms γ -FeSe as the thermodynamic product.

β -Fe_{1+x}Se exists in a relatively narrow phase width of $0.01 \leq x \leq 0.04$. β -Fe_{1+x}Se is a low-temperature superconductor with a critical temperature (T_c) of 8 K or below depending on the value of x .⁷⁹ The structure of β -Fe_{1+x}Se is an anti-PbO type structure with cubic close packed Se²⁻ with Fe²⁺ in half tetrahedral holes (Figure 2.14).

The tradition of synthesis of inorganic solids, including that of β -Fe_{1+x}Se, is that of a thermodynamic controlled process whereby the precise molar ratio of the raw elements, or equivalent, are ‘baked’ in the oven under high temperature for several days leading to the end thermodynamic product with the desired value of x .^{79, 80} Once synthesised, the value of x cannot be changed readily, or can it?

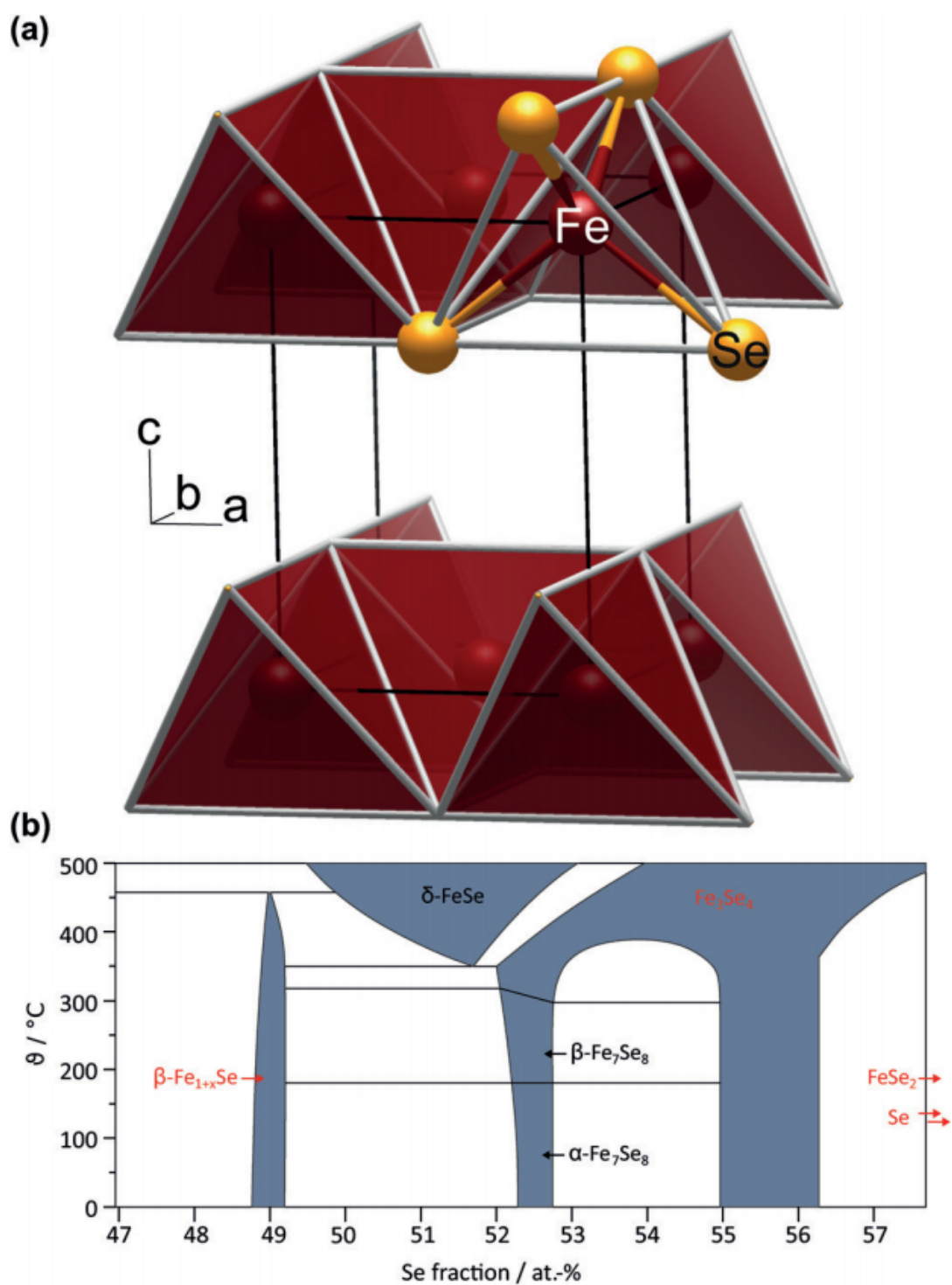


Figure 2.14 (a) Unit cell of the $\beta\text{-Fe}_{1+x}\text{Se}$ structure (anti-PbO type) (b) FeSe phase diagram in the vicinity of the 1:1 composition.⁸¹

In situ electrochemical X-ray diffraction experiments were conducted by immobilised $\beta\text{-Fe}_{1+x}\text{Se}$ onto an electrode, in the form of carbon/PVDF composite as above, in an oxygen-

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free cell containing pH 7.2 citrate buffer as the electrolyte. The three-electrode cell set up was completed with an Ag/AgCl reference and a graphite counter electrode. A slow scan rate of 1 mVs⁻¹ was deployed to allow diffusion of the pH buffering species into the composite (see indigo in Section 2.3.1) and to allow the structural changes to be tracked continuously by recording the X-ray diffraction patterns in situ (see Section 2.2.3 in Experimental). At key stages during the scans, samples were extracted for magnetisation measurements to determine the superconducting transition temperature - beyond the scope of this section - but nevertheless, it shows that the electrochemical products from this methodology can be easily collected for further post-analysis, see the published article for detail.⁵

Figure 2.15 shows the synchronised voltammetry and XRD data recorded during this experiment. The black line at the bottom of Figure 2.15 a) shows the potential waveform with time scanning from an open potential of -0.9 V (vs Ag/AgCl) to -1.25 V before reverting to +0.7 V; blue line is the current-time transient with a few key points (C1, A_{Fe}, A1 and A2) labelled for interpretation in conjunction with XRD patterns. The top part of Figure 2.15 a) shows the molar fraction of β -Fe_{1+x}Se (red) and selenium (blue) analyzed from in situ XRD patterns, as can be seen, the last oxidative peak in the reverse sweep A2 corresponds to the oxidative destruction of the β -Fe_{1+x}Se



The actual XRD patterns, 2 θ versus time, are shown in the top part of Figure 2.15 b) matching with an excellent agreement to the database XRD patterns of $\beta - FeSe$ and selenium.²⁸

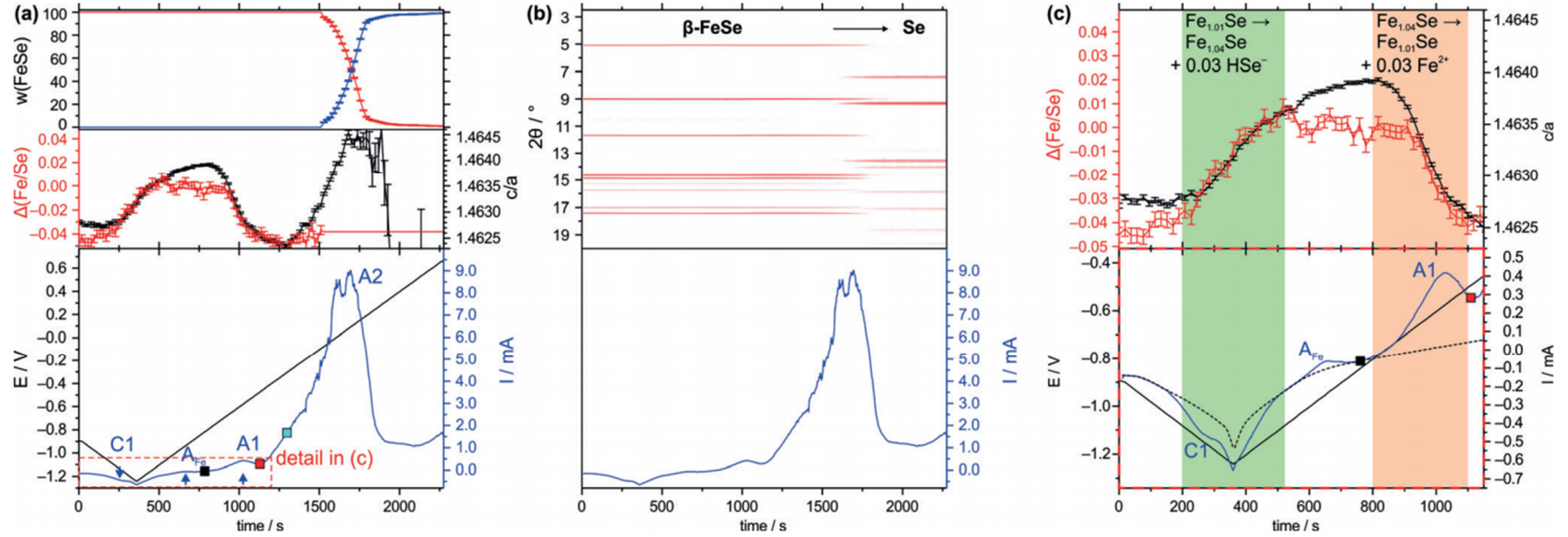
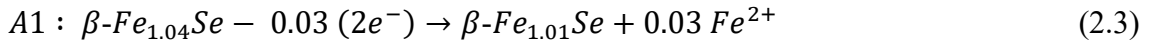
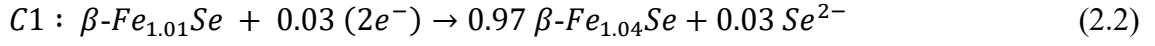


Figure 2.15 (a) Linear sweep voltammetry (LSV) at 1 mVs^{-1} with the potential being swept from -0.9 V to -1.25 V and to 0.7 V (bottom: black) with the current response (bottom: blue; dashed red rectangle see (c)), the molar fraction of $\beta\text{-Fe}_{1+x}\text{Se}$ (top: red) and selenium (top: blue), and the $\Delta(\text{Fe/Se})$ ratio (centre: red) and the c/a ratio (centre: black). The black, red and turquoise square mark the stages at which samples for the magnetisation measurements were extracted (see text). (b) Contour plot showing the strongest diffraction peaks and indices in the course of the LSV experiment (X-ray wavelength $\lambda = 0.494 \text{ \AA}$) with the current response from (a) as a guideline. (c) Zoom of the LSV experiment from (a) into the region of the partial oxidation of $\beta\text{-Fe}_{1+x}\text{Se}$.

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The small Faradaic signals observed (labelled C1, A_{Fe} and A1), prior to the oxidative destruction of the material (A2), are zoomed-in depicted in Figure 2.15 c). The Peaks C1 and A1, considering the phase width in Figure 2.14 b), are inferred to the following redox reaction from the initial $\beta\text{-Fe}_{1.01}\text{Se}$



This was deduced together by the charge ratio of peaks A1 to A2 leading to $\Delta x = 0.025$ with good agreement to the Rietveld refinement of the XRD patterns leading to $\Delta x = 0.04$.

The small signal labelled A_{Fe} on oxidation at -0.9 V is assigned to the oxidation of traces of elemental iron to Fe^{2+} , validated by experiments conducted additionally by Dr Rasche.⁵

To summarise, this section demonstrated the solid-state electrochemistry of the low-temperature superconductor, $\beta\text{-Fe}_{1+x}\text{Se}$, can be facilitated by the carbon/PVDF composite developed in this chapter. The highlight of methodology has presented in the in situ X-ray diffraction experiment revealing the electrochemical accessibility of the narrow phase width of $\beta\text{-Fe}_{1+x}\text{Se}$ post-synthesis. Furthermore, on oxidation we can separate the potential of this phase width from the that of the complete oxidation of $\beta\text{-Fe}_{1+x}\text{Se}$ to selenium and Fe^{2+} . The above firmly establishes the capability of this carbon/PVDF composite to extend phase width accessibility of (other) solid inorganic compositions post-synthesis.

2.4 Conclusions

A complementary method facilitating the electrochemical study of insoluble particulate compounds has been demonstrated in the chapter. By modifying a glassy carbon electrode with the carbon/PVDF composite containing the solid of interest, the overall mechanical rigidity, conductivity and porosity whilst binding the solid analyte to the electrode allows the solid-state electrochemistry to be studied over a large range of the aqueous solvent window; where the composite electrode remains stable and ‘intact’ under potentials as reductive as -2.0 V vs SCE .

The use of this carbon/PVDF composite offers several advantages over other solid-state electrochemical methods. In comparison to mechanical transfer methods, the carbon/PVDF composite utilises dropcasting to more accurately control the amount of reagents; comparative studies between experiments can therefore be made. Since the reactant is mostly embedded in the carbon/PVDF composite, the diffusion of the formed products into solution is hindered, and the reverse signal can be observed which otherwise might be lost with surface adsorption or abrasive methods. However, for electrochemical processes that involve the uptake of protons or hydroxide ions, the layers of carbon/PVDF can hinder the diffusion of species from bulk solution into the composite and thus may result in a slow buffering effect; the experimental conditions can be optimised to reduce this effect, by lowering the scan rate and reducing the dropcast volume for a thinner layer of carbon/PVDF composite – this allows longer time for the solution phase species to diffuse and across a shorter distance into the composite. A small reduction signal at -0.97 V vs MSE was attributed to residual atmospheric oxygen in the carbon/PVDF composite despite extensive outgassing of the solution; this was insignificant in oxygen-insensitive voltammetric studies but it is possible to overcome the problem by conducting

the fabrication process in an oxygen-free glovebox as shown in the β -Fe_{1+x}Se experiments.

Beyond initial electrochemical behavioural and characterisation of the carbon/PVDF composite in voltammetry, the composite was used as a rigorous method allowing the solid-state electrochemistry of α -HgS and β -Fe_{1+x}Se to be studied, each study with its own merit in scientific significance. Most notably, the mechanical rigidity of the carbon/PVDF composite and ease of modification allows the solid-state electrochemical experiment to be complementary studied simultaneously in situ with X-ray diffraction – pushing methodology beyond the traditional boundaries of electrochemistry. The in situ experiments can take place either inside a table-top X-ray diffractometer or a state-of-the-art synchrotron light source.

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Chapter 3 Insonation Leads to Concurring Formation of Molecular $\text{Hg}(\text{OH})_2$ and $\text{Hg}@\text{HgO}$ particles from a Mercury/Water Biphasic system

The use of electrochemistry in the chapter different to the approach in the previous chapter. Here, I first describe an unforeseen, but extraordinary observation that I stumbled upon during my DPhil, that is, what happens when one applies ultra-sound to a mercury/water biphasic system? Before my eyes – inside the fume hood and enclosed in a volumetric flask - ‘clouds’ of grey particles was seen emanating from the mercury/water interface within tens of seconds of sonication, as if a smoke grenade was set off inside the flask; visually, those grey clouds of particles were remarkably different from metallic, mirror-like $\text{Hg}(\text{l})$ droplets. Another surprise was that the grey particles did not unite with the liquid Hg when they sedimented. To a chemist, the colour change clearly indicated a chemical reaction.

Literature shows the above-described observation is not unprecedented, in fact, the observation was reported almost a century ago and it was thought that the grey ‘mercury emulsion’ was a result of the vigorous mechanical forces induced by the ultra-sound, analogous to what is seen in oil/water emulsification.¹⁻⁴ However, the electrochemistry experiments conducted herein shows the concurring sonochemistry was neglected.

The chapter begins with a short introduction and overview of the more recent progresses in sonochemistry which, below synergises with electrochemical observations; in particular, the widely accepted theory to the origin of another sonication induced phenomenon seen in water in the recent decades -

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‘sonoluminescence’. The electrochemistry presented in this chapter directly evidences and fingerprints the formation of a sonochemical product, molecular Hg(OH)₂, from insonation of mercury/water biphasic system. Moreover, a plausible explanation for the non-metallic coloured ‘mercury emulsion’ and the immiscibility with the liquid mercury is provided with support from X-ray diffraction patterns.

The research presented in this chapter lead to an open-access article published in *Chemical Science* – which granted full reuse permission for the purpose of this thesis.⁵ The authors who contributed to this work were interviewed by *Chemistry World Magazine* highlighting the broader significance of this work.⁶

3.1 Introduction

‘Acoustic cavitation’, the formation and collapse of bubbles suspended in a liquid can occur on exposure to intense sound fields with frequencies ranging from audible sound to ultrasound.⁷⁻⁹ When the bubbles collapse during the cavitation cycle photons are emitted with energies approximately eleven orders of magnitude higher as compared to the energy density of the sound field;¹⁰ this phenomenon, known as sonoluminescence, sparked interest throughout the scientific community with over 1000 papers published between 1990 to 2005.¹¹ This phenomenon can be found in nature, a snapping shrimps’ claw strikes at such a colossal speed so as to stun its prey it creates cavitation and subsequently light in the deep ocean – whimsically dubbed ‘shrimpluminescence’.^{12, 13} Nevertheless, the bubbles collapse near adiabatically, generating a ‘hot spot’ in which the temperature can reach 1,000 – 10,000 K with a pressure $> 10^7$ N m⁻².^{11, 14-16} Under these extreme conditions water molecules pyrolytically cleave to H· and OH·.¹⁷⁻¹⁹

Separate studies report OH· radicals, generated via photolysis of nitrate or methyl nitrite, can react with atomic mercury in both gaseous²⁰ and aqueous²⁰ phases as inferred indirectly from kinetic data with the possible formation of HgOH· and/or Hg(OH)₂ suggested. However, direct spectroscopic or other evidence for Hg(OH)₂ is sparse; an infra-red spectrum of Hg(OH)₂ deposited on solid Neon and Argon at 5K has been reported.²¹ It was thought that Hg(OH)₂ might play a role in the transport of inorganic mercury through lipid bilayer membranes.^{22, 23}

Metallic mercury at room temperature is immiscible with water. However, within tens of seconds of exposure to ultra-sound sonication, a grey ‘cloud’ of particles is seen emanating from the mercury-water interface into the aqueous phase.¹⁻⁴ The

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particles in the resulting mercury emulsion sediment within hours but do not re-merge with the bulk metallic mercury. Herein, we investigate the redox behaviour of the insonated mercury-water system, so as to generate $\text{OH}\cdot$ via acoustic cavitation, and explore the possibility of $\text{Hg}(\text{OH})_2$ formation. In particular, electrochemical methods evidence $\text{Hg}(\text{OH})_2$ in the solution phase which gives a voltammetric signature distinct from Hg^{2+} or Hg_2^{2+} .

3.2 Experimental

3.2.1 Chemicals

All chemicals used were of analytical grade and were purchased from Sigma-Aldrich (U.K) with the exception of metallic mercury purchased from Elgar Phosphors & Chemicals Ltd (U.K). All chemicals were used without further purification. Aqueous solutions were made using ultrapure water (Millipore, resistivity of 18.2 MΩcm measured at 25 °C). The saturated solution of Hg(OH)₂(aq) at 0.24mM was made by stirring solution containing the equivalent amounts of HgO(s) in 0.1M KNO₃ at an elevated temperature of 70 °C for 2 hours.²⁴

3.2.2 Electrochemical Cell

The electrochemical cell consists of three electrodes: a carbon microdisc working electrode (diameter = 7 μm, IJ Cambria Scientific Ltd, UK), a saturated mercury sulphate reference electrode MSE (ALS, Japan) and a carbon rod counter electrode. The electrochemical experiments were conducted with a computer-controlled potentiostat (BioLogic SP200, France). The working electrode was cleaned after each experiment using alumina slurries of decreasing particle sizes: 1.0, 0.3 and 0.05μm (Buehler, LakeBluff, IL, USA). All electrochemical experiments were thermostated at 25 °C.

3.2.3 Mercury Emulsion and Supernatant Separation

The ultra-sound sonication of 1 mL of metallic mercury in 100mL of aqueous 0.1 M KNO₃ was conducted in a SW1H Clifton ultrasonic water bath (37kHz, Nickel-Electro Ltd, UK). During sonication, a ‘cloud’ of grey particles is seen emanating from the mercury-water interface into the aqueous phase – please see the video

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available in the Additional Material named 'mercury emulsification.mp4'. The grey emulsion (termed a “mercury emulsion” in this chapter) was collected at sonication times of 5, 10, 15, 25, 40 and 60 minutes for electrochemical analysis. The grey particles were separated from the mercury emulsion via centrifugation (Eppendorf® Centrifuge 5702, Hamburg, Germany) at 4000 rpm for 5 minutes; the clear supernatant was then separated from the sedimented grey particles for further electrochemical analysis. An experimental scheme is shown in Figure 3.1.

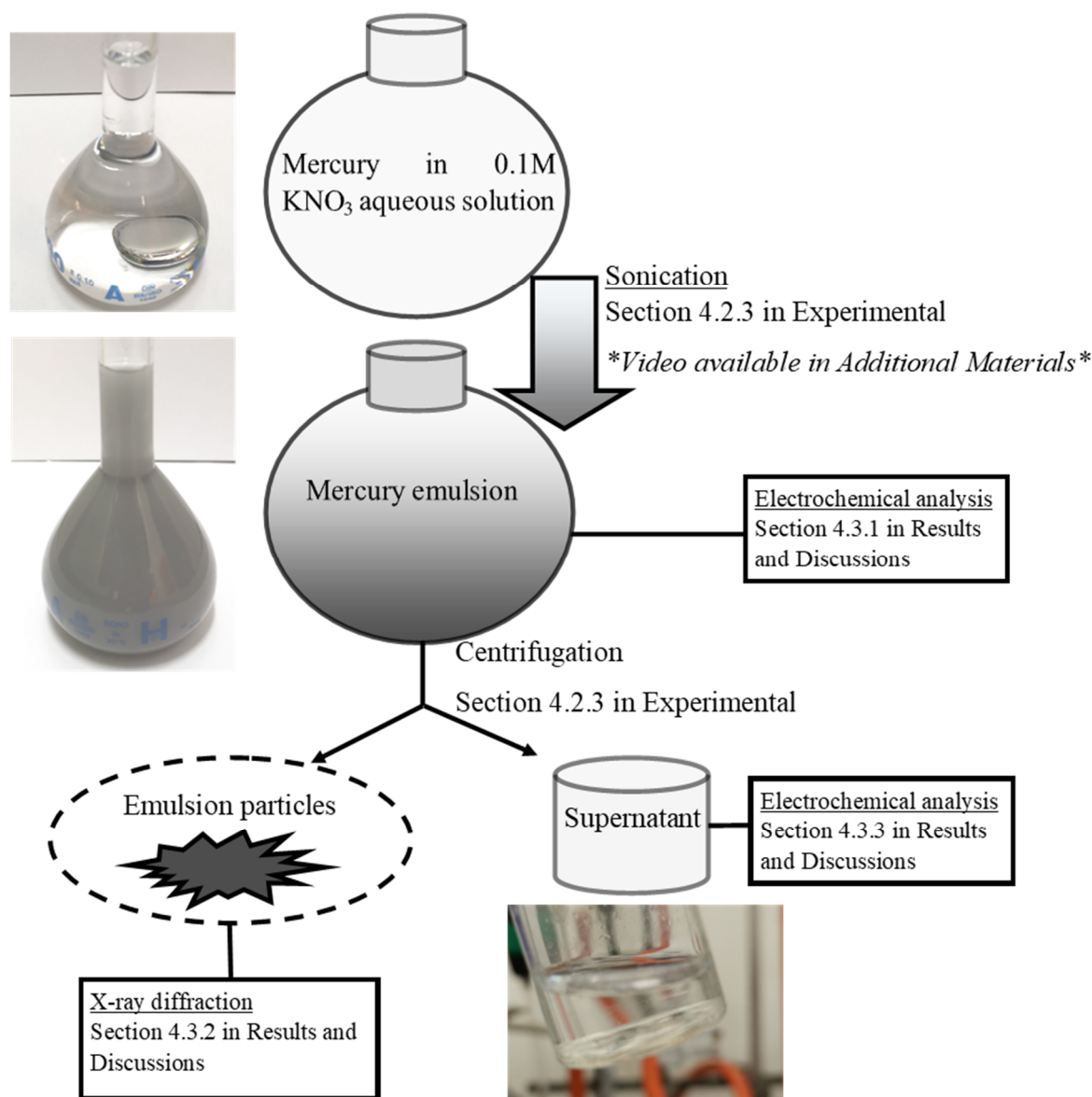


Figure 3.1. Experimental scheme.

3.2.4 X-ray Characterisation

The grey particles/particulates responsible for the emulsification were separated from the mercury emulsion by means of centrifugation. Moreover, since the original mercury/water system contains 0.1M KNO₃ electrolyte intended for electrochemical measurement, the separated grey particles were resuspended in deionised water and separated again by centrifugation, repeated three times, so as to wash off the electrolyte prior to X-ray diffraction experiments. Then, the sample was washed in ethanol and dried in air. X-ray diffraction was performed in a PANalytical Empyrean instrument operating in the Bragg–Brentano geometry with a curved Ge(111) Johansson monochromator to select Cu K α 1 = 1.54060 Å radiation with a step size of 0.013° 2 θ . The data was collected and evaluated by Dr Rasche using the WinXPow software.²⁵

3.3 Results and Discussions

The emulsification seen during insonation of a mercury/water biphasic system was studied via electrochemistry experiments. First, the cyclic voltammetry of the mercury emulsion is shown in Section 3.3.1 as a function of insonation time. The emulsion mixture was centrifuged to separate the grey mercury particles from the supernatant. Section 3.3.2 provides X-ray diffraction patterns of the mercury particles evidencing the formation of unreported Hg@HgO core-shell particles, thus explaining the non-metallic looking particles.

Section 3.3.3 shows the electrochemical experiments conducted in the supernatant solution evidencing an aqueous soluble and redox-active mercury species, albeit in the absence of grey mercury particles. The identity is fingerprinted in Section 3.3.4 as molecular $\text{Hg}(\text{OH})_2(\text{aq})$, which thus provides a plausible chemical linkage to the concurring formation of Hg@HgO core-shell particles during sonication.

3.3.1 Electrochemical Analysis: The Mercury Emulsion

A 0.1M KNO_3 aqueous solution containing metallic Mercury was sonicated for times of 5, 10, 15, 25, 40 and 60 minutes and the resulting mercury emulsion was collected. Figure 3.2 shows the resulting cyclic voltammogram (CV) recorded with a Carbon micro-disc electrode at a scan rate of 20 mVs^{-1} . The voltammograms were swept reductively from an initial potential of +0.5 V vs MSE with reversal from -0.6V. No Faradaic current was observed after 5 minutes of sonication time although emulsification was seen to occur within tens of seconds. After a sonication time of 10 minutes or longer, a quasi-steady state cathodic current with a half-wave potential around -0.26 V vs MSE can be seen, and approaches -0.9 nA after prolonged sonication times. The steady-state cathodic current on the

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microelectrode signals reduction of a solution phase species. During the reverse sweep, a near-symmetric “stripping” peak is observed at +0.05 V vs MSE and the peak height evolves over 60 minutes of sonication time. Furthermore, at higher oxidative over-potentials ‘spike-like’ voltammetric behaviour sporadically occurs. Those oxidative signals, the stripping peak and the ‘spikes-like’ events are only seen during the reverse sweep suggesting oxidation of reduction product(s).

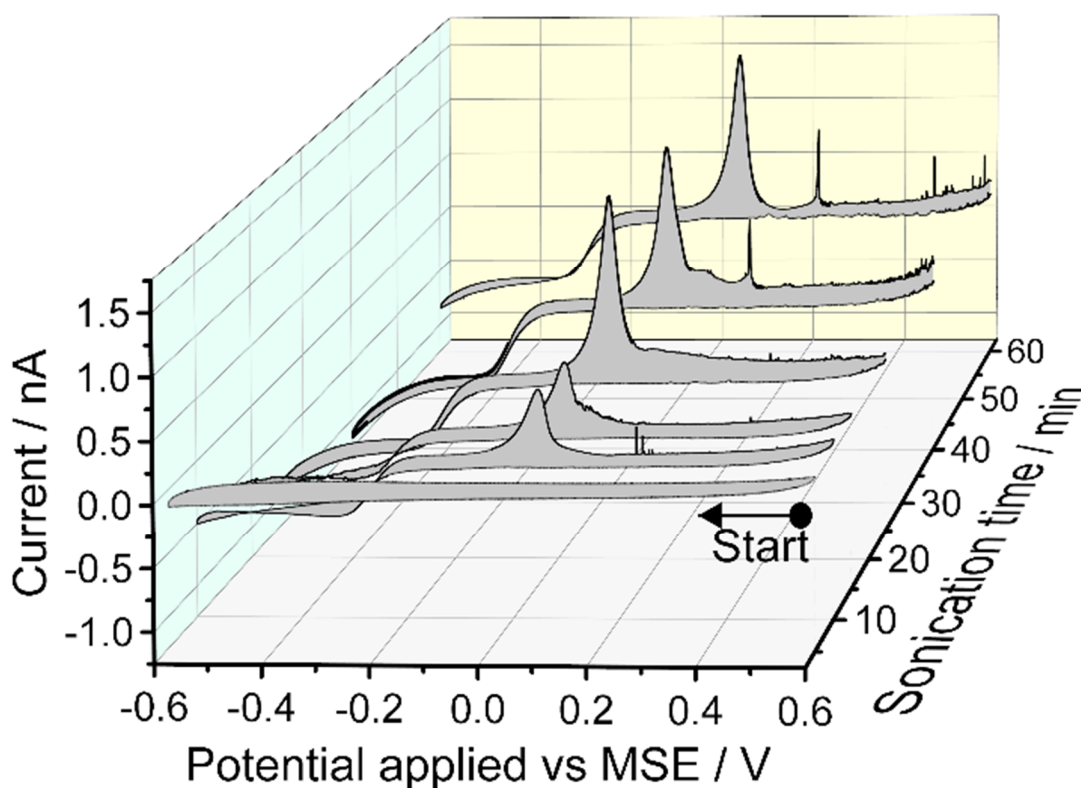


Figure 3.2. Cyclic voltammograms of the grey mercury emulsions generated by ultra-sound sonication of an aqueous solution containing 0.1 M KNO_3 and metallic mercury for 5, 10, 15, 25, 40 and 60 minutes. The voltammograms were recorded on a Carbon micro-disk electrode (diameter = 7 μm) at a scan rate of 20 mVs^{-1} .

Next, a series of double-step chronoamperometry experiments were conducted; first, the potential was stepped to a negative potential of either -0.8, -0.4, -0.2, or 0.0 V vs MSE for 30 s followed by a second potential step to an oxidative potential of +0.5 V for another 30 s. Figure 3.3 plots the current-time transients recorded during the second potential step. As can be seen, both the magnitude and frequency

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of the oxidative ‘spikes’ increases with the magnitude of the applied negative over-potential. Note the electrode was polished in between experiments to produce a fresh surface.

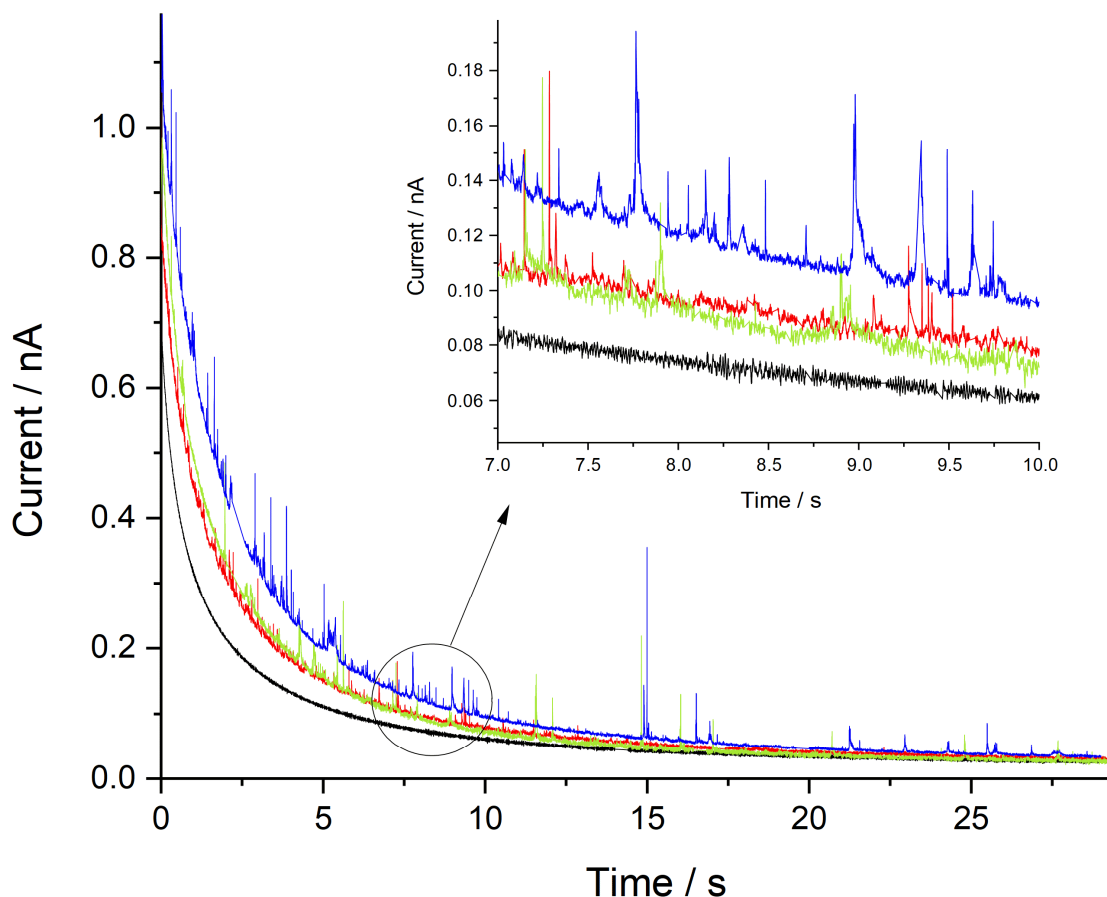


Figure 3.3. Chronoamperogram of the mercury emulsion with sonication time of 60 minutes. The potential step was first stepped to -0.8 V (blue), -0.4 V (green), -0.2 V (red) or 0.0 V (black) for 30 s then immediately to $+0.5\text{ V}$ for 30 s . Note the graph shows the current-time transient during the second potential step.

The spike charges in the double-step chronoamperometry experiment (Figure 3.3, blue line) were analysed. The size distribution of the mercury droplets is shown in Figure 3.4 with an average radius of $14.4 \pm 4.8\text{ nm}$ (calculated with the number of electrons transferred assumed to be $n = 2$ and also assuming the droplets are spherical in geometry and sufficiently small to undergo full oxidation).

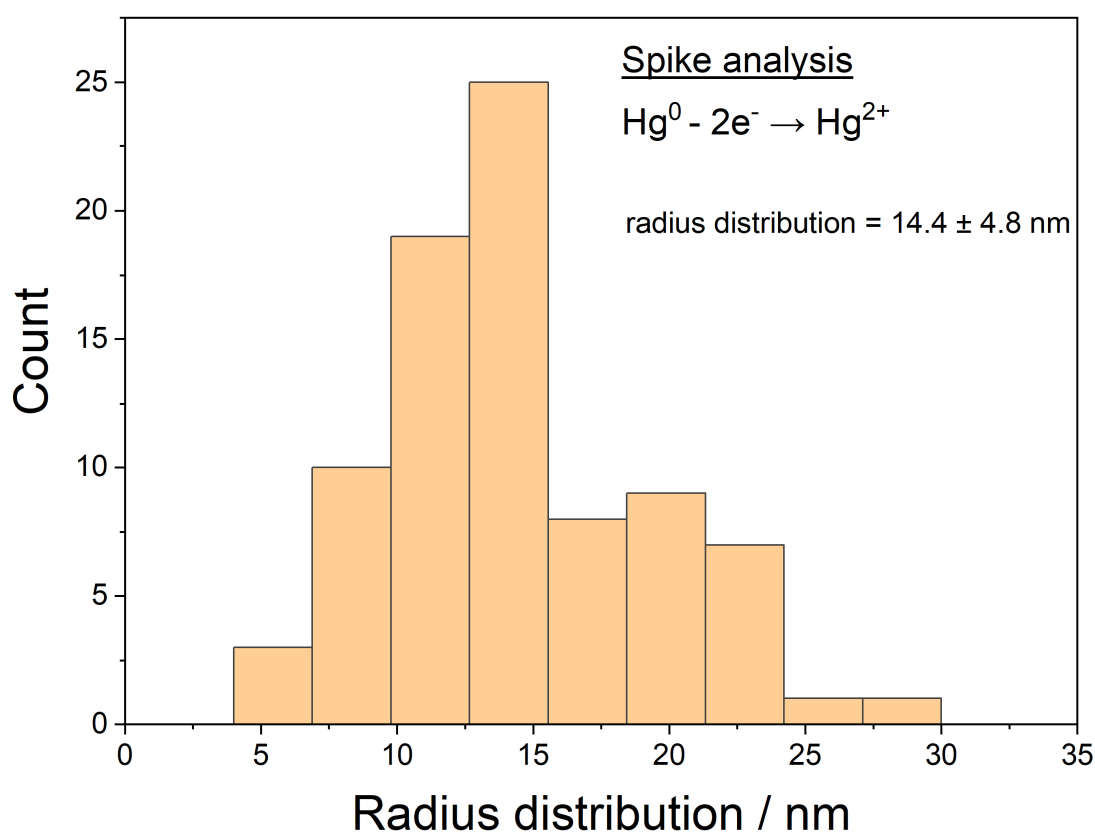


Figure 3.4. Size distribution of mercury droplets analysed from the double-step chronoamperogram shown in Figure 3.3, blue line.

Note that, the oxidative spikes are seen only after a negative potential ($< 0.0\text{V}$ vs MSE) was applied, as shown in Figure 3.3. Thus the observation is ascribed to the incomplete oxidation of bulk mercury resulting in the loss of small mercury droplets either into the solution phase, and/or remnants on the electrode surface, leading to the sporadic oxidation spikes. Further evidence is shown in Section 3.3.3.

In the next step, the X-ray diffraction patterns of the emulsion particles separated from the emulsification were analysed by Dr Rasche.

3.3.2 X-ray Diffraction: Hg@HgO Core-shell Particles

The grey emulsion/dispersion particles were isolated via centrifugation and the X-ray diffraction patterns (XRD) were measured and analysed. Figure 3.5 a) shows the XRD at room temperature (room temp) and two broad peaks at approximately

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33° and 66° (2θ) were seen which are fully consistent with that of liquid mercury reported in literature.²⁶⁻²⁸ However, additional peaks at approximately 9° and 25° (2θ) can be observed and do not belong to liquid mercury. The green line is the best fit to the broad amorphous diffraction peaks.

Upon prior heating the grey particles in air to 100°C , shown in Figure 3.5 b), the peaks of the liquid mercury vanish, and a sharp X-ray diffraction pattern emerges which corresponds to crystalline $\text{HgO}_{(\text{cr})}$ (*Pnma*, Pearson symbol oP8).^{29,30} Here, the purple line shows the line of best fit for the broad amorphous diffraction peaks after heating to 100°C . Nevertheless, the broad peaks around 9° and 25° 2θ remain. The peak at 9° 2θ is identified as amorphous scattering from the single crystal silicon sample holder (Figure 3.5 c), turquoise line). The peak at 25° 2θ is related to the isolated particles and is essentially unchanged on heating; it is attributed to amorphous $\text{HgO}_{(\text{am})}$. This can be seen by subtraction of the line of best fit for the amorphous peaks obtained after heating to 100°C (purple line) from that obtained in the absence of heating (room temp, green line), yielding amorphous peaks containing that of liquid mercury at room temp, shown in Figure 3.5 d).²⁶⁻²⁸

Therefore it is concluded that at room temperature the emulsion particles are composed of liquid Hg *and* amorphous $\text{HgO}_{(\text{am})}$, with the latter most likely forming a thin shell around the liquid Hg resulting in the matt grey appearance leading to the speculation that the shell prevents coalescence of the Hg droplets. After heating to 100°C HgO exists both in an amorphous and in a crystalline form. Note that Hg is lost on heating. To the best of our knowledge, this is the first XRD study of a mercury emulsion and the first to show that it consists of Hg and amorphous $\text{HgO}_{(\text{am})}$.

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The next sections turn to the electrochemical analysis of the supernatant in the absence of these Hg@HgO core-shell particles.

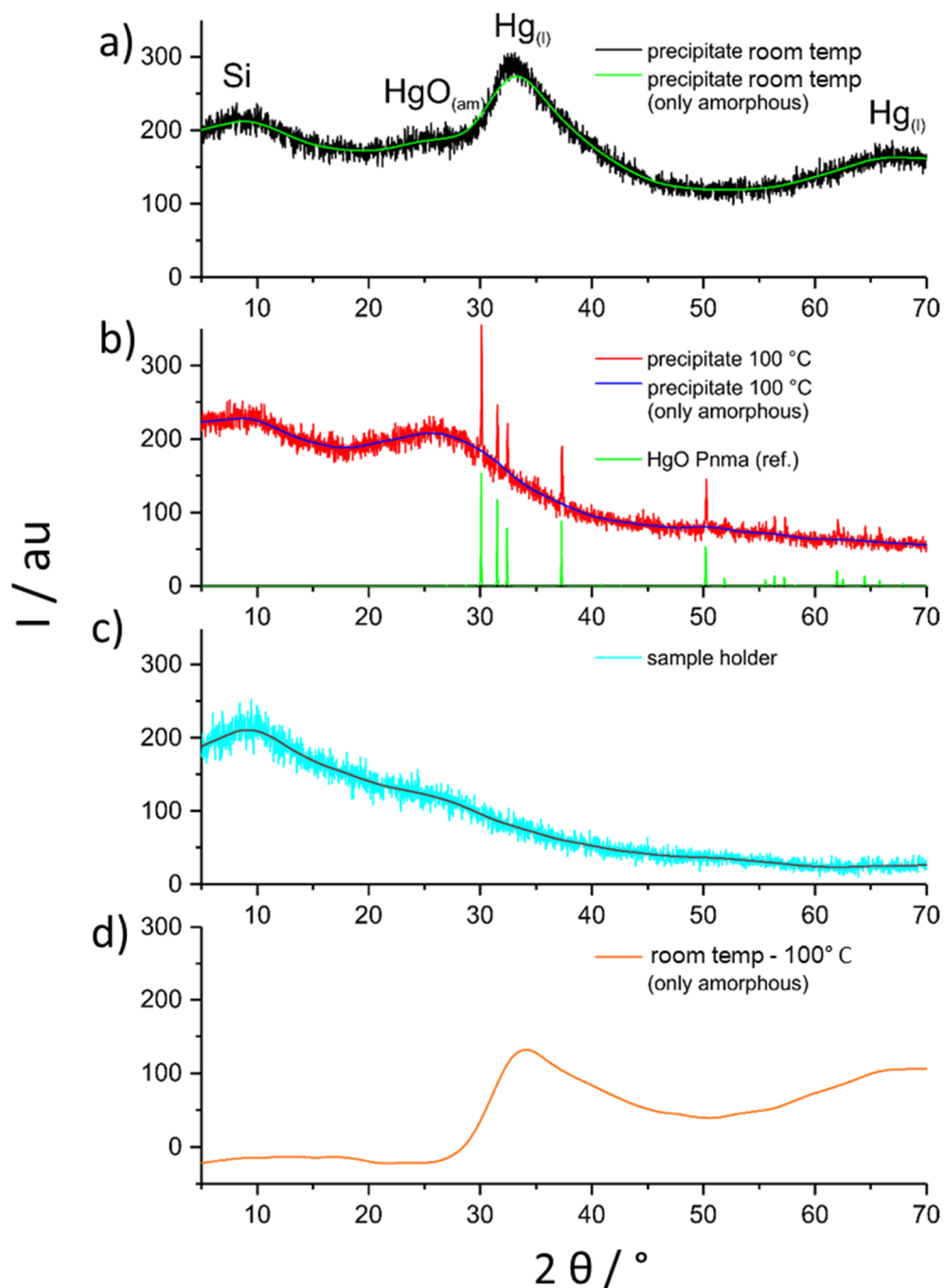


Figure 3.5. From top to bottom: X-ray diffraction data and the amorphous part of it (lowess filter) of the grey emulsion particles before (black, green), after (red, blue) heating to 100°C in air, from the silicon sample holder (turquoise, brown) and the difference between after and before heating (orange; only amorphous part). For the heated sample crystalline $\text{HgO}_{(\text{cr})}$ (green; Pnma, Pearson Symbol oP8) is shown as reference.³⁰ X-ray diffraction experiment and analysis credits to Dr Rasche.

3.3.3 Electrochemical Analysis: Supernatant

Figure 3.6 shows the cyclic voltammograms (CVs) of the supernatant solutions separated from the mercury emulsions prepared with different exposure times to sonication. Similar to the case of the mercury emulsion, presented in Figure 3.2, a quasi-steady state cathodic current is seen and with a magnitude approaches to -0.8 nA; a subsequent oxidation peak can again be seen at +0.05 V. Thus, this evidences a soluble mercury (I) or mercury (II) complex present in the solution phase after tens of minutes of sonication and this is independent of the presence of the grey particles which result from emulsification. The near symmetric oxidation peak at +0.05 V is attributed to the oxidation of Hg^0 at the electrode surface during the reverse sweep. Small oxidative spikes are seen and occur less frequently compared to the CVs obtained in the mercury emulsion (Figure 3.2).

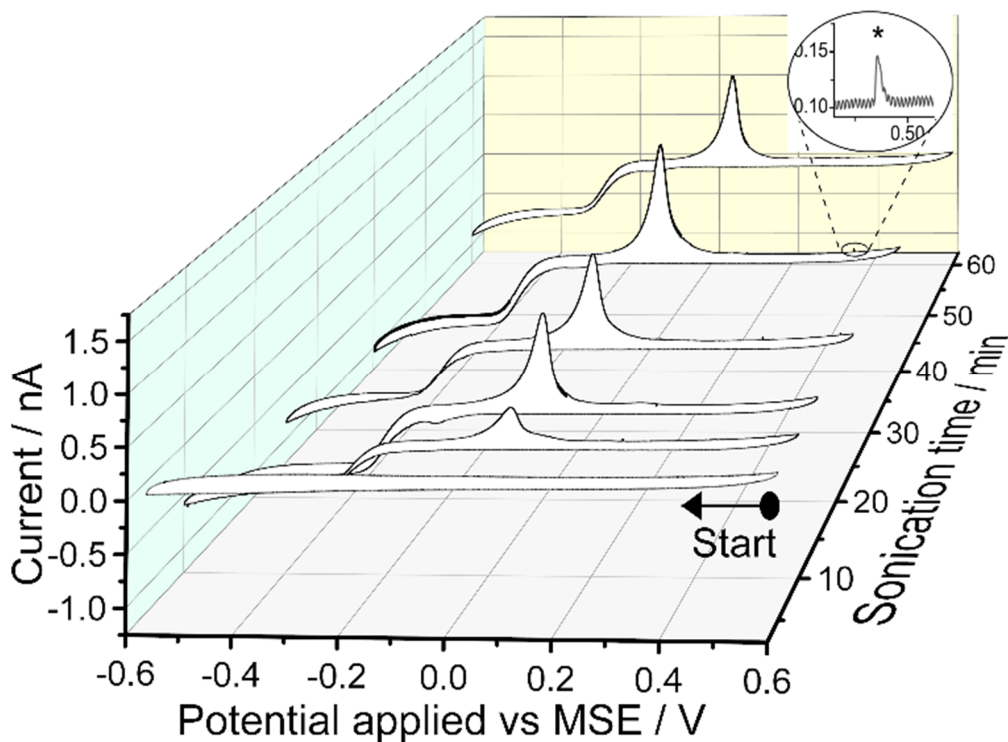


Figure 3.6. Cyclic voltammograms of the supernatant separated from the mercury emulsion after sonication. The supernatant solution was obtained by centrifuging mercury emulsions at 4000 rpm for 5 minutes. The voltammetric experimental conditions are the same as Figure 3.2. Inlay shows an examples of a small spikes().*

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Figure 3.7 shows the voltammograms of a ‘transfer’ experiment where a reductive sweep (black line) was first conducted in the supernatant. The electrode was then rinsed with deionised water and subsequently transferred to a 0.1M KNO_3 only electrolyte solution for “oxidative stripping” (red line). Both the stripping peak (E_{peak} at +0.05 V vs MSE) and the ‘spike’ events are seen, suggesting both oxidation processes resulted from surface-bound reduction products.

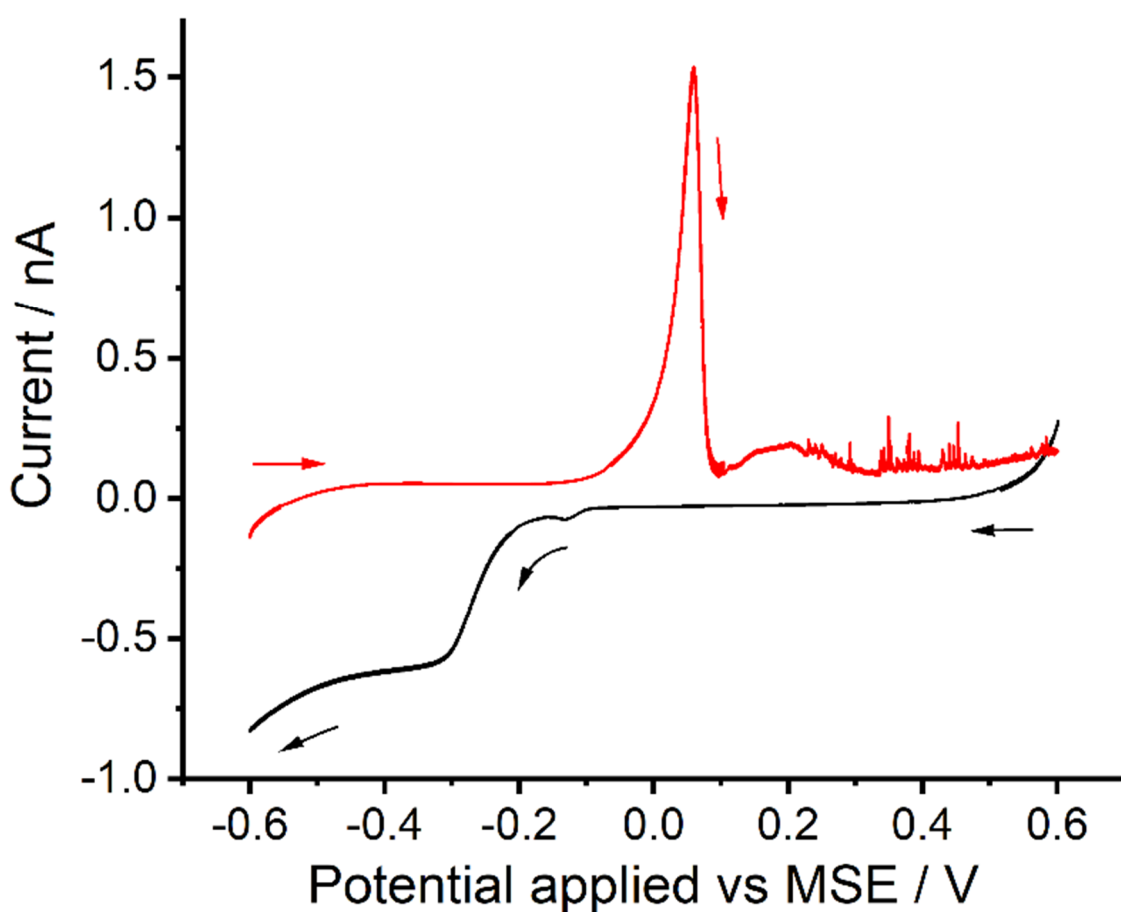


Figure 3.7. Transfer experiment conducted with the supernatant separated from a mercury emulsion after 60 minutes of sonication. Black line shows the reductive linear sweep voltammetry (LSV) recorded in the supernatant. Subsequently, the electrode was rinsed with deionised water and transferred to solution of 0.1M KNO_3 for oxidative sweep, shown as red line. Scan rate was 20 mVs^{-1} .

The physical origin of the spikes can be deduced from two of the above observations. First, the presence of mercury particles in solution, identified as $\text{Hg}@\text{HgO}$ core-shell in Section 3.3.2, does not lead to direct oxidative spikes

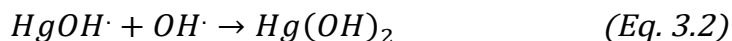
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unless a negative over-potential is first applied (Figure 3.3). Second, spikes are seen during the re-oxidation sweep in 0.1M KNO_3 electrolyte (transfer experiment, Figure 3.7). Thus, the ‘spike-like’ events are likely due to incomplete oxidation of surface-bound bulk mercury, resulting from the loss of small mercury droplets either into the solution phase, and/or as remnants on the electrode surface. These lead to sporadically occurring oxidation spikes as the droplets re-encounter the electrode or newly make electrical contact. As such these spikes are different in some respects to those seen in ‘Faradaic impact electrochemistry’ notably where nanomaterials, initially present in the solution, are either electrolysed directly or mediates a catalytic reaction as it diffuses to within a tunnelling distance from the electrode.^{31, 32} Furthermore, the size and frequency of the occurring spikes in CVs recorded in the $\text{Hg}@\text{HgO}$ core-shell particles containing emulsion solutions (Figure 3.2) are higher than that seen in the supernatant solutions (Figure 3.6), obtained under the same voltammetric conditions. A likely explanation is that the thin amorphous HgO shell layers surrounding the $\text{Hg}@\text{HgO}$ core-shell particles are reduced during the cyclic voltammetry, contributing their reservoir of core mercury to form more surface-bound mercury at the electrode surface.

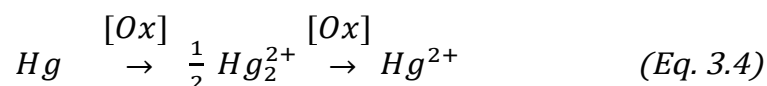
3.3.4 Electrochemical Analysis: Identity of the Aqueous Soluble Species

It is evident that a mercury (I) or mercury (II) complex soluble in the solution phase, after exposure to ultrasound, is electrochemically visible. The identity of this species is next considered. Plausible sonochemical reactions include first hydroxyl radicals $\text{OH}\cdot$ – formed via acoustic cavitation – reacting directly with Hg^0 to form soluble $\text{Hg}(\text{OH})_2(\text{aq})$ via Equations 3.1-3.3

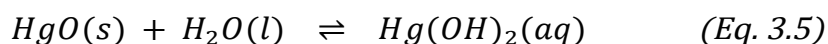
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and/or second, oxidation of elemental mercury Hg⁰, via electron transfer, by radical derived oxidants [Ox] to form Hg₂²⁺(aq) or Hg²⁺(aq) ions



where Ox might be OH[·], H₂O₂ or HOO[·] etc. Accordingly, we next compare and contrast the redox behaviour of the supernatant with solutions containing different mercury (I) or mercury (II) complexes. A solution of Hg(OH)₂ is thought to be obtained by dissolution of solid mercury(II) oxide



corresponds to a saturation limit of 0.24mM Hg(OH)₂.²⁴ Hg(OH)₂(aq) is known to not dissociate to Hg²⁺ and OH⁻.³³

Figure 3.8 shows four cyclic voltammograms obtained with the supernatant and three other mercury species. Overlaid in the top-half are the following: supernatant obtained after 60 minutes of sonication and the CVs from a saturated concentration of 0.24 mM Hg(OH)₂ obtained via dissolution of HgO(s). Overlaid in the bottom-half are CVs of 0.24mM of Hg₂(NO₃)₂ and Hg(NO₃)₂. In all cases, the potential was swept reductively from +0.6 V to -0.6 V vs MSE. For the supernatant solution, obtained after 60 minutes of insonation, a quasi-steady state cathodic current is seen approaching -0.8 nA as mentioned above. Similarly, the steady-state cathodic current for the saturated solution of Hg(OH)₂, obtained by dissolution of HgO, is

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close to -0.9 nA with a half-wave reduction potential seen around -0.28 V vs MSE (indicated by the grey dotted line). In comparison, the voltammetric signal for Hg₂²⁺(aq) and Hg²⁺(aq) – at equal concentration of 0.24mM - are distinctively different to that seen for Hg(OH)₂; first, the cathodic steady state current approaches to -0.6nA and second, a hysteresis/cross-over in current is seen in the voltammograms of Hg₂²⁺ and Hg²⁺. It is likely that deposition of mercury on a carbon surface changes both the electrode kinetics and surface morphology during the voltammetric sweep, thus leading to the reduction of Hg₂²⁺ and Hg²⁺ ions at higher oxidation potential on the reverse sweep.

It is evident that, insonation of a mercury-water system generates soluble Hg(OH)₂, which is visible voltammetrically. Moreover, as discussed in the introduction (Section 1.4.3), the magnitude of the steady-state current I_{ss} recorded on a micro-disk electrode is directly proportional to the concentration (C) and diffusion coefficient (D) of the analyte

$$I_{ss} = 4nFDc_{bulk}r_e \quad (Eq. 3.6)$$

where n is the number of electrons transferred, F is the Faraday constant and r_e is the radius of the micro-disc electrode. Thus, a diffusion coefficient of Hg(OH)₂, $1.4 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, in aqueous solution at 298K can be deduced from the saturated Hg(OH)₂ solution, obtained via dissolution of HgO, with a known concentration of 0.24 mM.

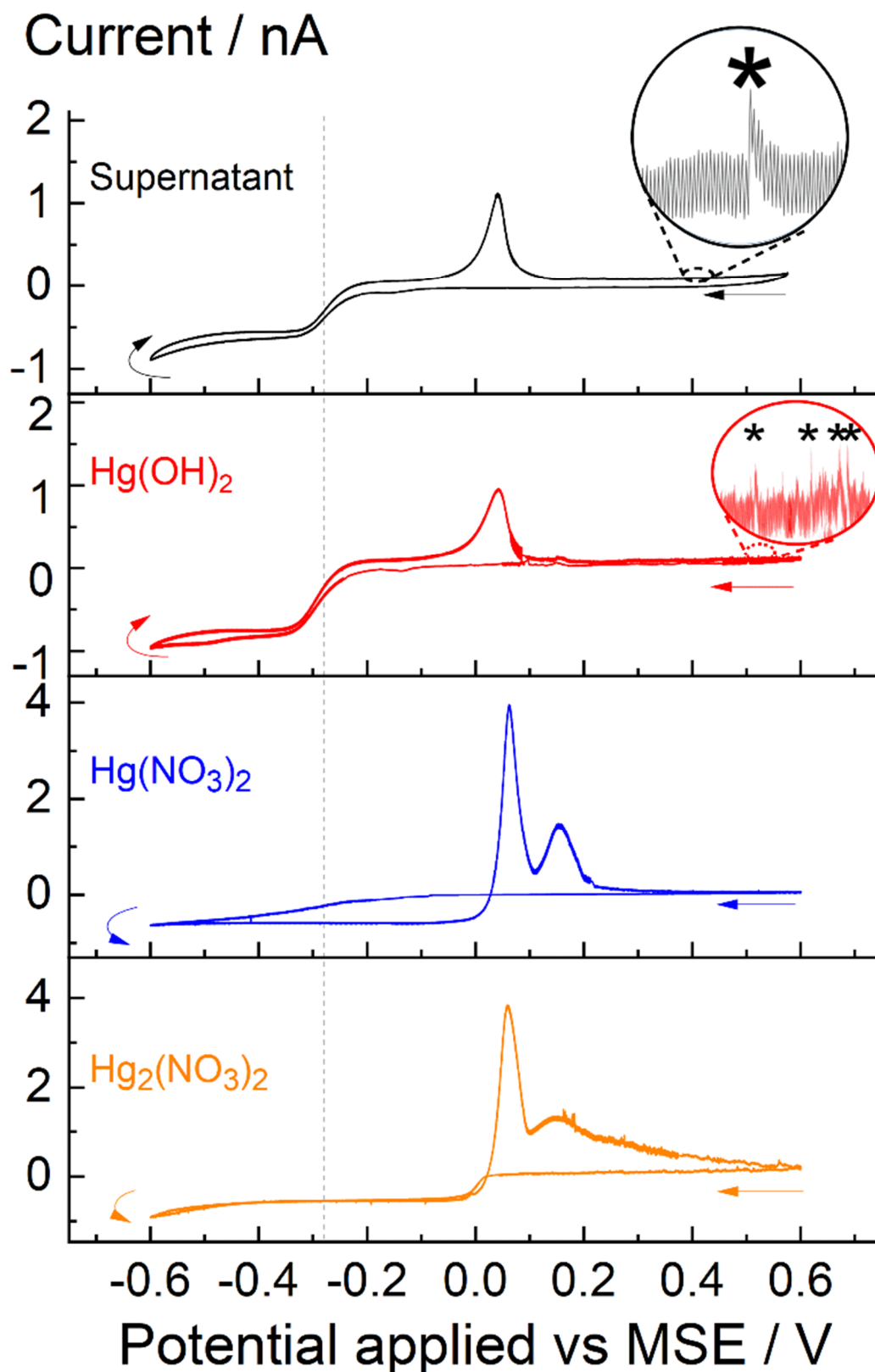


Figure 3.8. Cyclic voltammograms various mercury (I) or mercury (II) ion containing 0.1M KNO_3 solutions. Black line – supernatant obtained after 60 minutes of sonication; red line –saturated solution of $\text{Hg}(\text{OH})_2(\text{aq})$ obtained via dissolution of 0.24mM HgO ; blue line – 0.24mM $\text{Hg}(\text{NO}_3)_2$; orange line - 0.24mM $\text{Hg}_2(\text{NO}_3)_2$. The grey dotted line indicates the half-wave potential at -0.28V. Inlay shows examples of small spikes(*).

3.4 Conclusions

Insonation of mercury/water system leads to grey emulsions in which the particles have been characterised as Hg@HgO core-shell structures. Further, a molecular mercury species in the solution phase - after insonation of mercury/water system - is voltammetrically visible and characterised as that of Hg(OH)₂, a possible intermediate in the sonochemical formation of HgO. The voltammetric signatures of Hg(OH)₂ are distinctively different from the freely solvated Hg₂²⁺ and Hg²⁺ ions, with noticeably different half-wave potentials and an absence of hysteresis in the current during the reverse sweep. Moreover, the steady-state cathodic current of - 0.8 nA recorded with the supernatant, obtained after 60 minutes of insonation, suggest a concentration of Hg(OH)₂ approaching the saturation limit of 0.24 mM at 298K.

The formation of molecular Hg(OH)₂ is consistent with both the ‘hot spot’ model for the generation of OH· via cavitation leading to concomitant reactions with elemental mercury to form Hg(OH)₂, *and* the XRD evidences of Hg@HgO core-shell particles. The structure of the latter provides an explanation to the non-metallic, grey appearance of the ‘emulsification’ *and* lack of coalescence with liquid mercury upon sedimentation.

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Chapter 4 Susceptibility of Phytoplankton Towards Oxidative Damage

This chapter presents a multi-disciplinary, but at core electrochemistry project involving marine phytoplankton. Unlike the previous two chapters which investigated inanimate inorganic materials, the electrochemistry in this work directly probes the resiliently-living, micron-sized and single-celled photosynthetic phytoplankton which are globally important – they are the nutrition sources for all life in the ocean; more of which is discussed in the introduction.

The electrochemical work demonstrated in this chapter is novel and is a proof-of-concept in developing a rapid and cost-effective fluoro-electrochemical sensor for the speciation of phytoplankton in the ocean. Here electrochemistry is combined with in situ fluorescence microscopy imaging thus allowing the response of individual phytoplankton towards electrochemically induced oxidative stress to be optically visualised and quantified via the fluorescent photosynthetic chlorophyll pigments. At high oxidative potentials, without chemical additives, the electro-generated species in artificial seawater is shown to drastically change the chlorophyll fluorescence intensity. While this electrochemically generated species are identified as hydroxyl radical via multiple approaches, the work further extend to studies a total of six different species of phytoplankton so as to develop a proof-of-concept for a ‘susceptibility library’ for speciation based on oxidative chemical attack.

The results presented in this chapter were published in the journal *Chemical Science*,¹ which has granted full reuse permission for the purpose of this thesis. All experimental results and analysis presented in this chapter were conducted by the present author unless

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otherwise stated. Contributions were made by Ms Y Guo (RGC group), Dr Q Zhang (Rickaby group, Oxford) and Dr L Chen (RGC group) in culturing and monitoring the population of phytoplankton, essentially keeping them alive and ‘healthy’ for the experiments presented herein.

4.1 Introduction

The denomination phytoplankton is a broad catch-all term encompassing a range of single cellular microorganisms spanning twelve taxonomic divisions and includes both Eukaryotes and Bacteria. Over 5000 species of phytoplankton² have been identified with sizes ranging from 1 μm to over 100 μm . However, all phytoplankton cells contain chlorophyll-a (chl-a) which absorbs light and is used for the conversion of dissolved inorganic carbon (e.g. $\text{CO}_2(\text{aq})$) to organic molecules such as carbohydrates, lipids and proteins.³ Although individual phytoplankton are microscopic, they are responsible for approximately half of the photosynthesis on Earth, and are the conduit through which energy enters aquatic ecosystems. There is currently an active debate regarding the extent to which global phytoplankton biomass may have declined over the previous century;^{4, 5} this has serious implications for the global marine ecosystem. Phytoplankton cells can achieve high densities in the natural environment that alter the colour of the surface ocean, which can be viewed in satellite images.⁶ These images can be used to remotely measure the scale and density of a phytoplankton bloom.⁷⁻⁹

Beyond the use of chl-a fluorescence to estimate phytoplankton biomass, the time variation of the cellular chl-a fluorescence intensity may also be used to yield insight into the photosynthetic performance of phytoplankton.^{10, 11} Fast repetition rate fluorometry¹² allows, amongst other parameters, the photochemical conversion efficiency and the photosystem II functional absorption cross-section to be analysed. Such cell physiology measurements, in combination with the assessments of cell growth, are a common route by which the effects of cellular oxidative stress are investigated.¹³ In terms of species identification and cell density estimation, both at sea and in the laboratory, flow cytometry is a primary technique;¹⁴ where the relationship between side scatter versus

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fluorescence intensity is used to identify the presence of different plankton species. This procedure is however not without limitations; problems arise when species have similar optical properties or when single species display a wide size range due to cell agglomeration and chain formation.¹⁵

Reflecting the fact that phytoplankton occurs in a number of taxonomic divisions, their composition, shape and size vary widely between species. For example, *Emiliana huxleyi* is a representative species of the calcifying phytoplankton; such plankton produce plates of calcium carbonate inside their cells which are extruded onto their external cell walls. These calcifying plankton species play a critical role in the oceanic carbon cycle.¹⁶⁻¹⁹ Despite being energetically costly,²⁰ it has been proposed that calcification in return offers coccolithophores physical protection, reduces UV damage, and potentially accelerates photosynthesis.^{21, 22} In contrast, diatoms are encased in a siliceous skeleton and play a key role in the transport of carbon to the ocean's interior.²³ The morphologically diverse green algae are cosmopolitan members of aquatic ecosystems and may be important contributors to primary production in productive marine and freshwater environments.²⁴

In clear water solar UV radiation penetrates to a depth of 10-20 m.^{25, 26} The susceptibility of phytoplankton towards solar radiation damage has been previously reported, where the sensitivity of different species is often interpreted on an allometric (cell size) basis.^{27, 28} Beyond direct radiation damage, UV light is also able to photolyse nitrate, nitrites and other chromophoric dissolved organic matter present in the ocean; these photoreactions are a major source of hydroxyl radicals in the marine environment.²⁹ Furthermore, at the air-water interface, the transfer of atmospheric hydroxyl radicals to the water has also been evidenced to be an important source of oxidising radicals.³⁰ Once transferred or

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formed in the aqueous phase, these highly reactive hydroxyl radicals will lead to the formation of other reactive species such as carbonate radicals.²⁹ Highly oxidising and reactive species are potentially deleterious for aquatic life.³¹

Radical species can be formed not just photochemically but also electrochemically. Hydroxyl radicals can be generated on a large scale via a strong electric-field gas discharge (kV) to eliminate invasive marine species in ship's ballast water;³² microscopic marine species such as phytoplankton and bacteria were shown to be killed within tens of seconds.³³⁻³⁶ On a small scale, high potentials at carbon electrodes can oxidise water and/or the ions present in solution ("solvent breakdown"). Although at these high potentials the formation of oxygen from water is thermodynamically favourable, the process involves multiple steps; consequently, in the absence of a suitable oxygen evolving catalyst such as a metal oxide,^{37, 38} significant quantities of reactive intermediates (such as hydroxyl radicals, $\text{OH}\cdot$) will be formed. At pH 7 the electrode potential for the one-electron oxidation of water to the hydroxyl radical is +2.07V (vs Saturated Calomel Electrode, SCE).³⁹ Hence, in accordance with the Nernst equation and assuming reversibility of the electrode process, the formation of concentrations of hydroxyl radicals as high as millimolar may be favourable at around ~1.9 V (vs SCE). Notably, the direct one-electron oxidation of hydroxide occurs at significantly lower potentials of 1.3 V vs SCE on gold electrodes;⁴⁰ likely due to stabilisation of the intermediate, $\text{OH}\cdot$ radicals, on surface adsorption sites.

This chapter studies the interaction between phytoplankton and electrochemically formed highly oxidising species using fluorescence electrochemical microscopy. We primarily focus on the study of six phytoplankton in four different groups, namely a diatom (*Halimnion coffeaeformis*), a coccolithophore (*Emiliana huxleyi*), the eustigmatophyte

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Nannochloropsis oceanica and three freshwater green algae (*Stichococcus bacillaris*, *Chlorella singularis* and *Chlorella volutis*). Also investigated is a representative dinoflagellate (*Scrippsiella trochoidea*), however, study of this species was somewhat limited by its low cell density (below 10^3 per ml in contrast to 10^6 per ml for the above-described species). The results evidence the widely different sensitivity of phytoplankton species towards strongly oxidising environments, and indicate that the differences reflect the different physical and chemical composition of the shells and outer membranes of the phytoplankton.

4.2 Experimental

This chapter provides additional information on the ‘upkeep’ of the phytoplankton culture, a description of their cell composition from a chemist’s perspective and the bespoke fluoro-electrochemical cell set up.

4.2.1 Chemicals

All chemicals used were of analytical grade and were purchased from Sigma-Aldrich, with the exception of NaF which was purchased from Fluka. All chemicals were used without further purification. Aqueous solutions were made using ultrapure water (Millipore, resistivity of 18.2 MΩ cm measured at 25 °C).

4.2.2 Phytoplankton Culture

The *Halamphora coffeaeformis* (diatom, CCAP 1001/2), *Stichococcus bacillaris* (freshwater algae, CCAP 379/1A), *Chlorella singularis* (freshwater algae, CCAP 211/119), *Chlorella volutis* (freshwater algae, CCAP 211/120) and *Nannochloropsis oceanica* (marine algae, CCAP 849/10) was obtained from Scottish Marine Institute, Scotland. The *Emiliana huxleyi* (coccolithophore, RCC 174) and *Scrippsiella trochoidea* (dinoflagellate, RCC 91) was sourced from the Roscoff Culture Collection (RCC), France. The phytoplankton were cultured under 16 hours of light and 8 hours of dark cycle at 22°C. The medium used here was largely following the recipe of f/2 medium from the Bigelow National Centre for Marine Algae and Microbiota (USA), but used synthetic ocean water instead of natural seawater. The synthetic ocean water was prepared following Morel *et al.*⁴¹ The culture which the freshwater algae were grown in (3N-BBM+V) were exchanged with f/2 medium prior to the electrochemical experiments.

4.2.3 Phytoplankton Structures: From a Chemist's Perspective

This work studies a range of different phytoplankton species – a diatom (*Halamphora coffeaeformis*), a coccolithophore (*Emiliania huxleyi*), three freshwater green algae (*Chlorella singularis*, *Chlorella volutis* and *Stichococcus bacillaris*), a marine algae (*Nannochloropsis oceanica*) and a dinoflagellate (*Scrippsiella trochoidea*). All species are visible under the light microscope and are approximately 2-25 μm in diameter.

Shown in Figure 4.1 are scanning electron microscopy images of three phytoplankton species. The diatom *H. coffeaeformis*, shown Figure 4.1 a) and with permission to reuse from Elsevier,⁴² is bilaterally symmetric in shape and consists of a porous silica frustule cell wall.^{42, 43} Behind the cell wall lies the chlorophyll-a containing plastid (Mereschkowsky's type 2) - characteristic for the 'H' shape under fluorescence conditions.⁴² Coccolithophore *E. huxleyi*, shown Figure 4.1 b), is enclosed in detachable liths of calcium carbonate and appears spherical under the epi-fluorescence microscope. Interestingly, the life cycle of *E. huxleyi* contains three phases; the commonly known, non-motile and coccolith forming C-cell, the non-motile and 'naked' N-cell, and the motile scale-covered S-cell.⁴⁴ Both N-cells and S-cells may appear spontaneously in a culture of C-cells.⁴⁵ Dinoflagellate *S. trochoidea*, shown Figure 4.1 c) and with permission to reuse from Wiley & Son,⁴⁶ has a cellulose-based cell wall and is significantly larger (~25 μm). Under a light microscope, with a magnification up to 400x, diatoms, dinoflagellate and coccolithophores can be easily differentiated from each other due to their unique shape and size.

All the green algae under study and *N. oceanica* are spherical in shape with the exception that *S. bacillaris* is oval in shape. The cell wall composition of the algae is commonly in the form of cellulose.

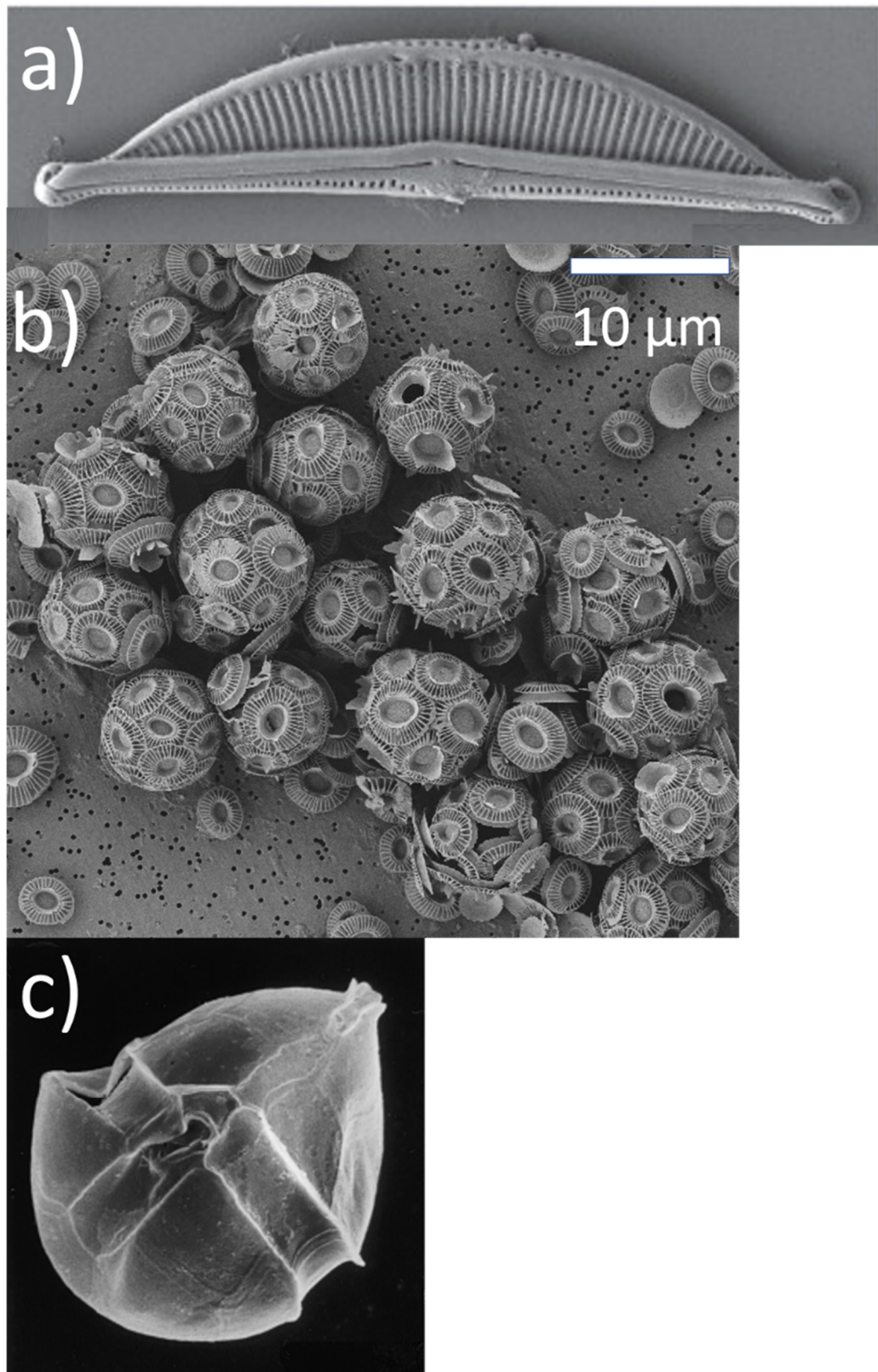


Figure 4.1. Scanning electron microscopy images of three species of phytoplankton in this article: a) diatom *H. coffeaeformis*;⁴² b) coccolithophore *E. huxleyi*; c) dinoflagellate *S. trochoidea*.⁴⁶ Reuse permission for SEM images in a) and c) was granted from Elsevier and Wiley & Son, respectively. Scale bar of 10 μm applies to all three species shown.

4.2.4 Fluoro-electrochemical Cell and Set Up

To facilitate the in situ fluoro-electrochemical experiments, a bespoke thin-layer cell was designed and build in-house by the author. The fluoro-electrochemical thin-layer cell, shown schematically in Figure 4.2, consists of three electrodes with two carbon fibre wires (diameter 7 μ m, Goodfellow Cambridge Ltd.) which act as working and counter electrodes, and a silver epoxy coated carbon fibre wire function as a pseudo-reference electrode. The cell depth is roughly 50 μ m. Potentiostatic control and synchronization with the camera was provided within a previously developed device,⁴⁷ built in-house by Dr C. Batchelor-McAuley, and uses a current-amplifier (Keithley 427, US).

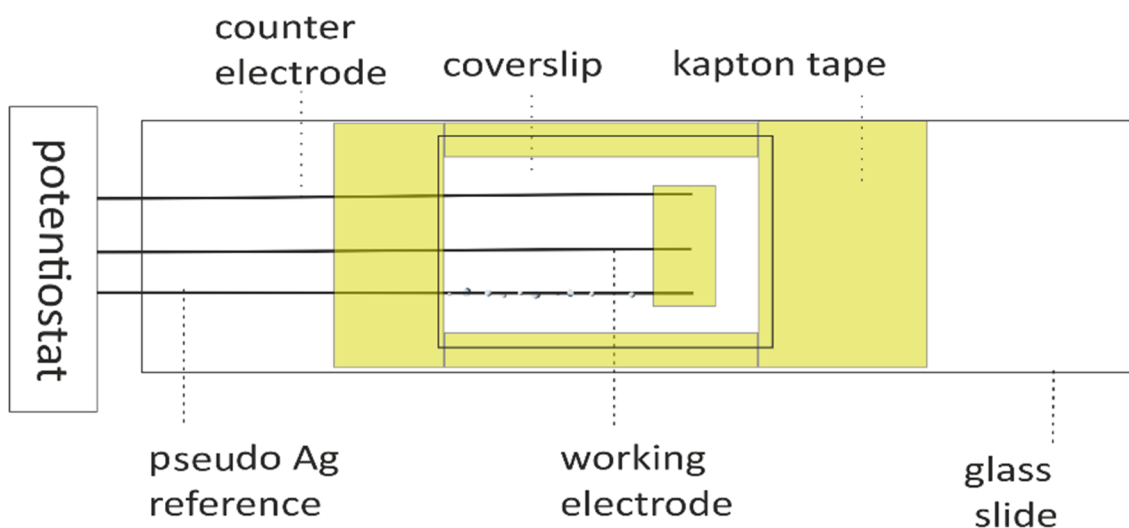


Figure 4.2. Schematic of the thin-layer fluoro-electrochemical cell.

4.2.5 Microscope and Image Analysis

The fluorescence excitation light source was provided by a LQ-HXP 120 V lamp. Optical measurements were made on a Zeiss Axio Examiner, A1 Epifluorescence microscope (Carl Zeiss Ltd., Cambridge U.K.) using a 20x air objective (NA = 0.5, EC Plan-Neofluar) and 40x oil immersion objective (Plan-Apochromat 40x/1.3 Iris (UV)VIS-IR). The excitation filter was purchased from Thorlab (FITC 475 $\pm$ 35nm); the dichromic mirror and emission filter were from Zeiss filter set 15 which transmit emission wavelengths

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above 590nm. The video acquisition was provided by a Hamamatsu ORCA-Flash 4.0 digital CMOS camera (Hamamatsu, Japan), providing 16-bit images with 4 megapixels of resolution. The intensity extractions were performed in Zen 2 pro.

4.2.6 Videos of the Fluoro-electrochemical Experiments

Uploaded in ‘Additional Materials’ are three microscope videos of the phytoplankton in the thin-layer electrochemical cell. The video descriptions are given below:

Phytoplankton – Video One(.mp4); this video depicts the oxidative response of the diatom *H.coffeaeformis* to a potential step of +2.3 V. The video has been taken under epi-fluorescent illumination; hence the diatoms appear as bright spots in the optical field. The position of the working electrode is schematically indicated on the video. The video is displayed at 5 times faster than real-time.

Phytoplankton – Video Two (.mp4); this video depicts the electrochemical response of three different phytoplankton species in a thin-layer electrochemical cell again under epi-fluorescent illumination. These three species were selected for their ease of identification under the microscope as is evident in the video. The video is displayed at 3 times faster than real-time.

Phytoplankton – Video Three (.mp4); this video depicts the oxidative response of a dinoflagellate (*S. trochoidea*) and a diatom (*H. coffeaeformis*) towards a strongly oxidising potential of +2.3V. In this video both epi-fluorescent illumination and a low level of transmitted light has been used. The footage was also taken using a higher (x40) magnification oil immersion objective. Hence, in this video the electrode appears as a dark band across the top of the image. The larger size of the dinoflagellate and the use of the transmitted light allows the phytoplankton internal structure to be observed whilst

simultaneously allowing the change in plankton fluorescence response to be monitored. The video is displayed at 3 times faster than real-time.

4.2.7 Analytical Method: Second Derivatives of the Intensity – Time Plots

The fluorescence intensity time transients of the phytoplankton (as depicted in Figure 4.5) measured in the fluoro-electrochemical experiment were analysed using the second derivative of intensity (with respect to time) to obtain the “onset time” after which the phytoplankton fluorescence were affected upon applied of the electrode potential. The black dotted line in Figure 4.5 shows the natural fluorescence decay of the diatom upon the light being switched on - this decay is known to be associated with the self-protection mechanism of the chlorophyll-a containing photosystem II to prevent photochemical induced cellular damage.⁴⁸ For the first 60s, the fluorescence light is switched on and the fluorescence intensity approaches a near steady-state. At $t = 60$ s, or onset time of 0, the electrode potential steps to +2.3V. To obtain an estimate for time at which the electrode potential starts to influence the phytoplankton fluorescence intensity, the second-order derivative of the intensity with respect to time is calculated and plotted in Figure 4.3. The *minimum* of the second derivatives corresponds to the point of *greatest change* of the gradient of intensity with time and are used to determine the ‘onset time’ for the fluorescence decrease.

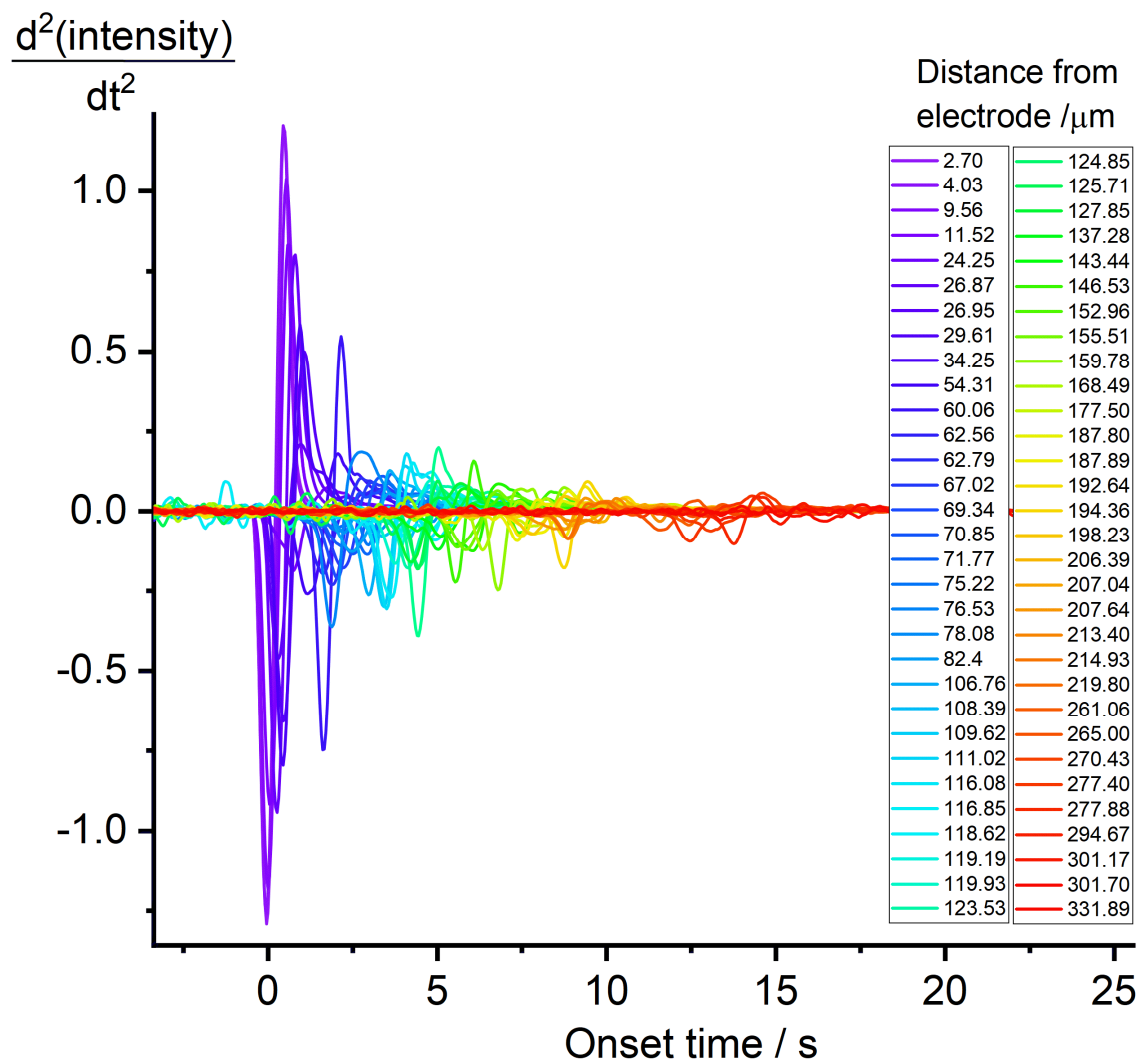


Figure 4.3. A plot of the second derivative of the intensity-time plot shown in Figure 4.5. A Savitzky–Golay filter with 2nd order of polynomial fitting and 20 points of window was used to calculate the second derivative. The x-axis is plotted as the ‘onset time’ which is the time from $t = 60\text{s}$.

4.3 Results and Discussion

All phytoplankton species selected for study in this work have length scales in the range of 2-20 μm . The plankton can be visualised under a fluorescence microscope (excitation wavelength of 475 ± 35 nm and the emission by-pass above > 590 nm) due to their strong fluorescence response arising from the presence of chl-a in the cells. However, these species differ markedly in their cell structure, the diatom has a porous silicate shell, the coccolithophore can be found encased in a shell of calcium carbonate and the algae have cellulose-based cell walls (see Section 4.2.3).

First, the electrochemical induced biological behavioural change in phytoplankton, reflected by their chl-a fluorescence, will be discussed in detail for a representative species of diatom (*H.coffeaeformis*). Then, the results are extended to a wide variety of phytoplankton in demonstrating the possibility of developing a ‘susceptibility library mapping’ of phytoplankton towards electrode oxidative stress.

4.3.1 Diatom

Response to Electrochemically Generated Oxidising Species

This work starts by studying the response of the diatom *H. coffeaeformis* in a fluoro-electrochemical cell. Figure 4.4 depicts a series of fluorescent microscope images for *H. coffeaeformis* extracted from the fluoro-electrochemical experiment. The bright features present in the optical field are the phytoplankton present either as individuals or in larger agglomerates. These diatoms are held in a thin layer cell (ca. 50 μm depth) which also contains a carbon fibre electrode ($r_e = 3.5$ μm). The cell also contains counter and reference electrodes. A schematic of the cell is shown in Section 4.2.4. These carbon fibre electrodes are non-fluorescent and hence are not observable under the epi-fluorescent illumination conditions. In Figure 4.4, the position of the carbon fibre wire is indicated

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by the blue line across the microscope image; the reference and counter electrode are out of view. Initially, a potential of 0.0 V was initially applied to the electrode for 60s and a series of microscope images recorded at 10 frames per second. At this potential (0.0 V) no Faradaic reactions occur at the carbon fibre electrode. After 60 seconds the applied potential is stepped to an oxidative potential of +2.3 V (vs pseudo Ag wire) with a steady-state current approaching 60 μ A recorded on a centimetre long micro-cylinder electrode, the chronoamperogram is reported in Appendix: A. The series of images shown in Figure 4.4 are of the thin-layer cell taken at different times *after* the onset of the higher potential (please see the video available in the Additional Materials named ‘Phytoplankton – Video One.mp4’, a description of the video is in Section 4.2.6.). As can be seen from Figure 4.4 the fluorescence response of *H. coffeaeformis* closest to the electrode are ‘switched off’ first and the fluorescence associated with the diatoms further away from the electrode progressively decrease with increasing time. Note that after the experiment, the fluorescence response shows no signs of increase over a period of an hour; thus, the *H. coffeaeformis* are considered irreversibly damaged by the electro-generated species. To understand this electrochemical potential induced oxidative damage, the data embedded in the experimental video file including the pixel intensity, distance per pixel and time were all extracted and quantitatively analysed.

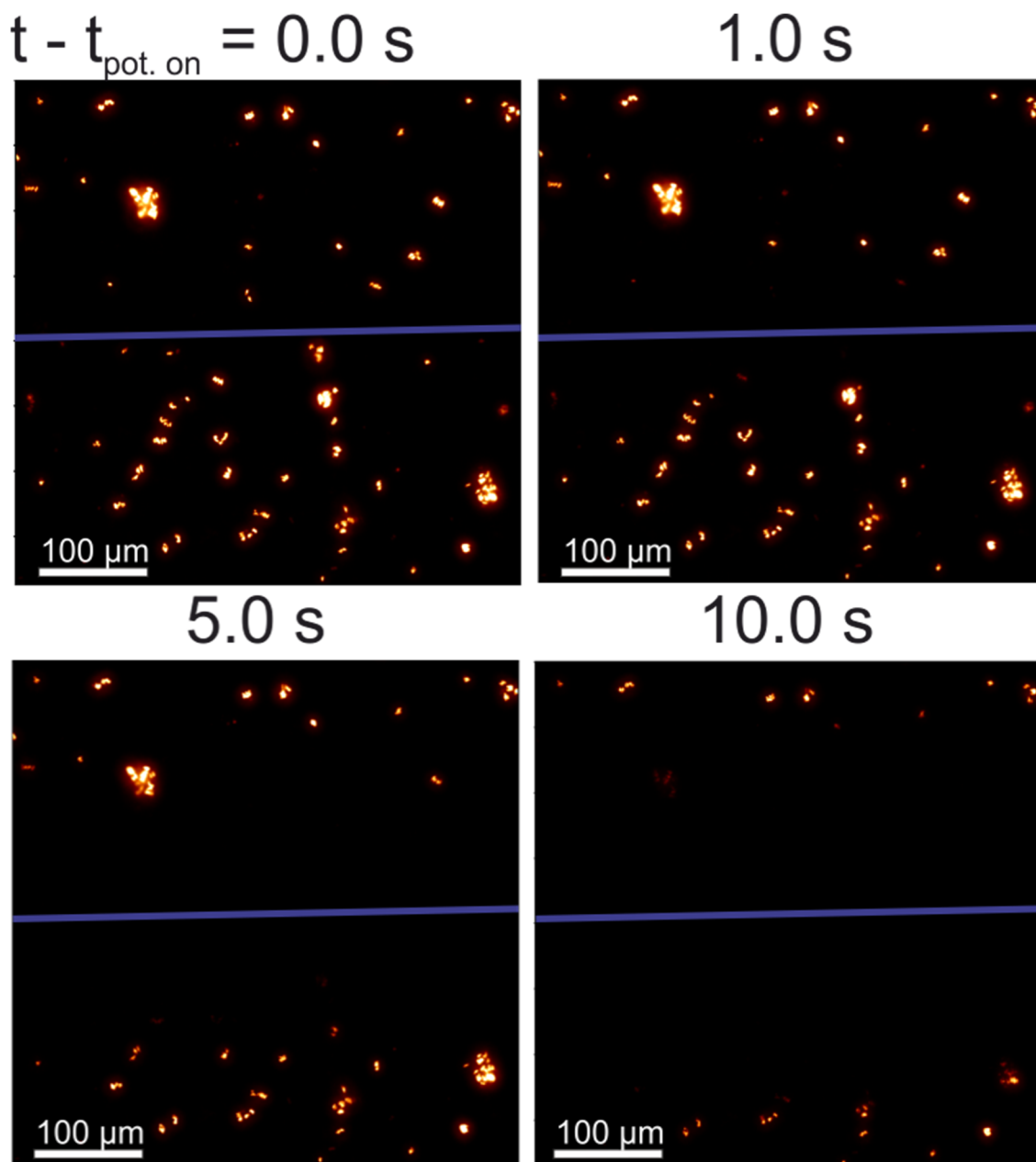


Figure 4.4 . Optical images of the chl-a fluorescence of *H. coffeaeformis* (diatom, CCAP 1001/2) during the fluoro-electrochemical experiment, where $t_{\text{pot. on}}$ is the time which a potential step of 2.3 V (vs pseudo Ag wire) was applied to the working electrode. $\lambda_{\text{ex}} = 475 \pm 35 \text{ nm}$ and $\lambda_{\text{em}} > 590 \text{ nm}$. The blue line depicts the location of the carbon fibre electrode. A potential of 0 V (vs pseudo Ag wire) was applied for $t = 0 - 60 \text{ s}$, before the potential steps to 2.3 V for $t = 60 - 90 \text{ s}$. The chl-a fluorescence signals are coloured as gold-yellow for contrast.

The fluorescence response of individual phytoplankton were measured over the entire plankton cell via integration of the microscope image to obtain mean fluorescence intensities per plankton. The perpendicular distances between different plankton and the electrode were also measured and found to be in the range of $2 \mu\text{m}$ to $330 \mu\text{m}$. Figure 4.5

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shows the integrated fluorescence intensity of 62 individual *H. coffeaeformis* cells as a function of time; the fluorescence intensity has been normalised against its value recorded at $t = 0$ s and each trace in Figure 4.5 is for a different diatom. The fluorescent transients depicted in Figure 4.5 are colour coded according to the individual's distance from the electrode, from blue (closest, 2.7 μm) to red (furthest 331.9 μm). At $t = 0$ s, the epi-fluorescent light source is turned on, and then after 60 seconds a strong oxidising potential (+2.3V) is applied to the working electrode.

As can be seen, after the epi-fluorescent light is turned on there is an initial rapid decrease in the fluorescence intensity of the diatoms. After 40 seconds of illumination, the diatom fluorescence intensity decreases to approximately 35% of its original value. Note this initial decrease in the fluorescence intensity is not related to the occurrence of any reaction at the electrode surface but is due to the high light intensity used as part of the epi-fluorescent microscope setup. This decrease is well known⁴⁹ and is associated with the plankton protecting themselves from photochemically induced cellular damage.⁴⁸ The black dotted line overlaid in Figure 4.4 shows the measured fluorescence response of a representative *H. coffeaeformis* diatom where an oxidising potential has **not** been applied at 60 seconds.

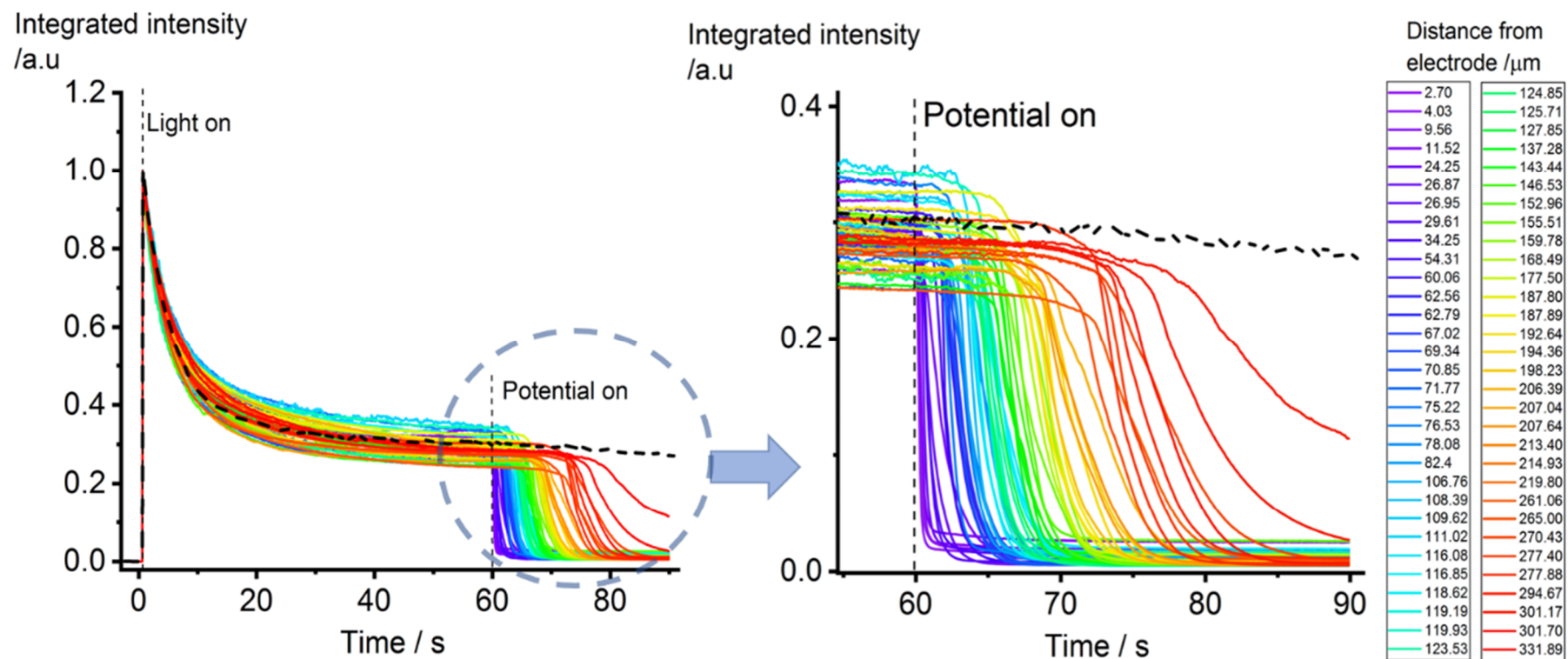


Figure 4.5 a) Normalised fluorescence intensity of individual *H. coffeaeformis* (diatom, CCAP 1001/2) located at different distances from the electrode during the fluoro-chronoamperometry experiment. A potential of 0.0 V (vs pseudo Ag wire) was applied from $t = 0 - 60$ s, before the potential steps to 2.3 V for $t = 60 - 90$ s. The colour transient from blue to red illustrates an increase in perpendicular distance of the corresponding diatom from the electrode ranging from $2\mu\text{m}$ to $330\mu\text{m}$. The black dotted line is the fluorescence decay of *H. coffeaeformis* in the absence of applied potential. b) zoom-in for $t = 60 - 90$ s.

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Here it is clear; although the fluorescence intensity initially decreases over the course of 90 seconds following irradiation, the fluorescence intensity is relatively invariant soon after 40 seconds. The intensity profiles deviating from the control experiment, in the absence of oxidative potential, is directly inflected by the applied potential from $t > 60\text{s}$ causing the fluorescence to rapidly ‘switch-off’ as a function of distance from the electrode. As can be seen from the images shown in Figure 4.4, the diatoms are stationary over the timescale of the experiment with no physical contact to the electrode. From this one can infer it is the chemical product(s) of the electro-oxidation process that diffuse away from the electrode and inhibit the phytoplankton fluorescence at a greater distance from the electrode with time.

The relationship between the onset time for the fluorescence ‘switch-off’ with distance is quantified using the analytical procedure described in section 4.2.7. Figure 4.6 a) plots the time at which the phytoplankton fluorescence intensity decrease is initiated against the distance squared; the results shown come from three separate experiments highlighting the reproducibility of the system. At short times, shown in Figure 4.6 b), a quasi-linear relationship with a gradient of $3.0 \times 10^{-9} \text{ m}^2\text{s}^{-1}$ can be seen. However, at longer distances, a deviation from the initial gradient is seen; an explanation is provided by a theoretical model developed by Dr C. Batchelor-McAuley shown in Appendix: A. In brief, due to the necessary requirement of the reactive species diffusing away from the electrode surface before they can react with and induce damage to the phytoplankton, the resulting measured fluorescence response arises from a convolution of multiple physical and chemical factors. The deviation from the initial gradient seen in Figure 4.6 at a longer distance from the electrode are explained by a threshold quantity, or to simplify, a threshold concentration of the electrogenerated species, above which lead to the

destruction of the cellular structure and initialises the decay in chl-a fluorescence intensity.

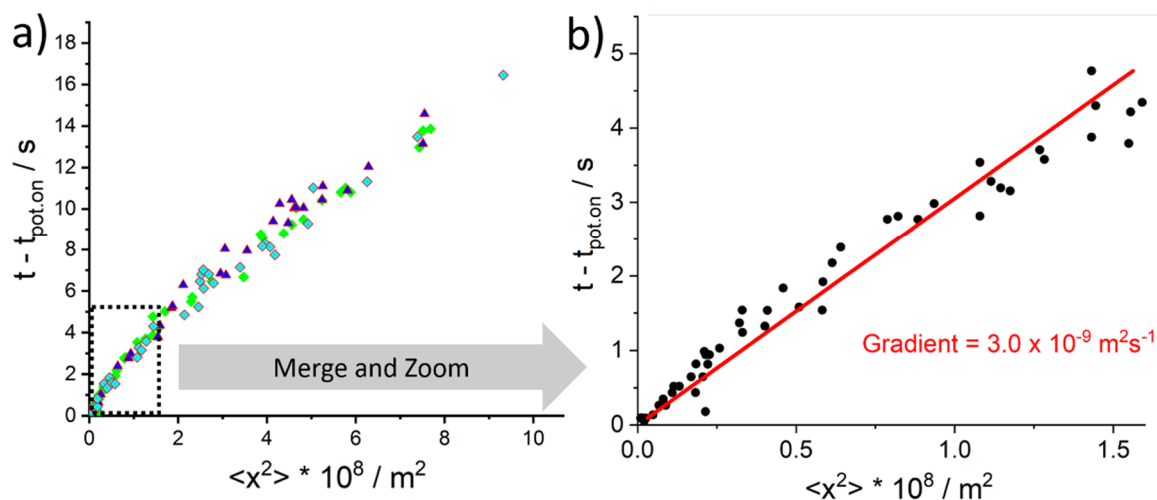


Figure 4.6 Plot of time taken for the diatoms to respond to the applied potential of +2.3V (vs pseudo Ag wire) versus the corresponding diatom's perpendicular distance away from the electrode square. a) data analysed from 3 repeated experiments; b) zoom-in and with all data point, over the 3 repeats, shown collectively as black circles and the corresponding linear line of best fit is shown in red.

The question to pose next is, to what extent does the magnitude of the potential effect the chl-a switch-off and which electrogenerated chemical species are responsible for chl-a inhibition? The next two sections begin to answer those questions by first repeating the same experiment, each with a unperturbed culture of *H. coffeaeformis*, but using a different onset potential at $t = 60\text{s}$ so as to narrow down the potential range of product formation.

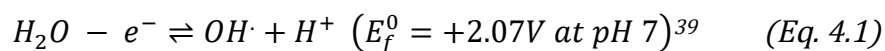
Chemical Identity: Electrode Potential Dependency

Figure 4.7 shows three plots of the intensity time transient with different potentials applied to the electrode at 60s; namely 2.0, 1.7 and 1.4V (vs pseudo Ag electrode). Qualitatively, the fluorescence intensity transients with an applied potential of 2.0V are comparable to those recorded at 2.3V; over the course of the experiments the fluorescence intensity of the diatoms within 300 μm of the electrode were affected by applied potential.

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At a lower oxidative potential, however, the rate of fluorescence switch-off decreases and the diatoms further away from the electrode are not significantly affected. For a potential step of 1.4V, with in the same time scale, only the diatoms within $\sim 60\mu\text{m}$ of the electrode are significantly affected by the electrochemically generated species. Moreover, the fluorescence of the phytoplankton were not affected by reductive potentials as negative as -2.0V.

Certainly, one feasible electrochemical reaction within the potential window of +2.0 to +2.3 V (vs pseudo Ag wire) is the oxidation of water leading to the formation of hydroxyl radicals. As discussed in the introduction, a potential of $\sim +1.9\text{V}$ (vs SCE) on the basis of the Nernst equation is required for a favourable electrochemical formation of millimolar concentration of hydroxyl radicals at pH 7



$$1.9 \approx 2.07 - \frac{RT}{F} \ln\left(\frac{1}{1 \times 10^{-4}}\right) \quad (\text{Eq. 4.2})$$

Previous work in the literature has shown both in-vivo and in-vitro that strongly oxidising radical species, such as the hydroxyl radical, can cause the oxidative destruction of chl-a.⁵⁰ Thus, the observations seen at lower applied potentials maybe the result of insignificant electrochemical driving force for radical production. The next section provides direct spectroscopic evidence by chemical reactions of the diatom with a homogeneous solution containing a range of other feasible electro-chemical product(s).

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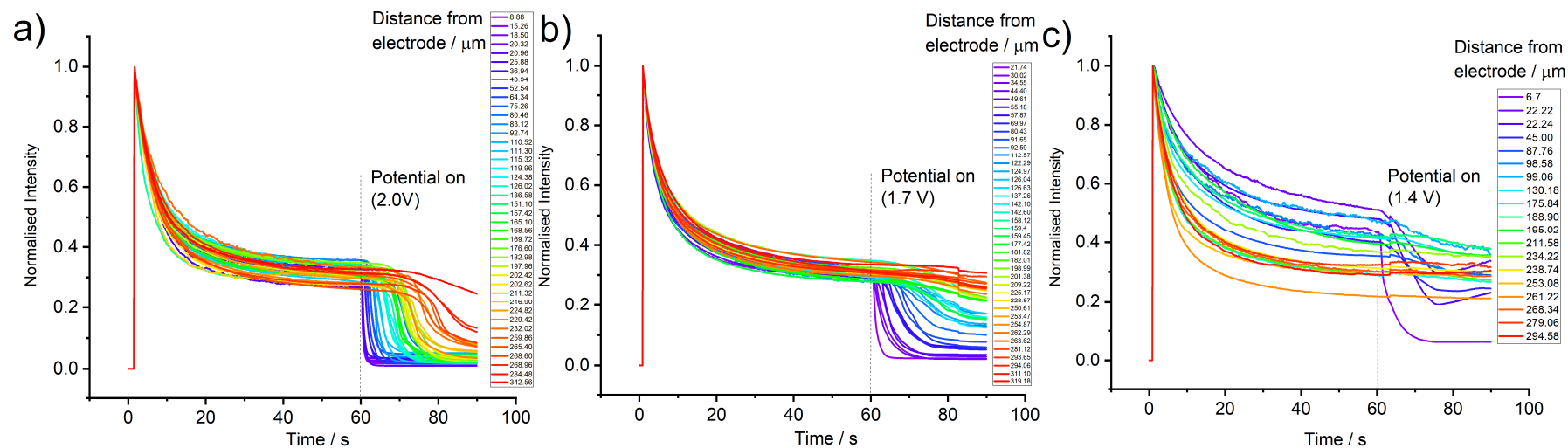


Figure 4.7 The fluorescence intensity of diatom in the fluoro-electrochemical experiment. An applied potential of 0V was applied for 0-60s. At $t = 60$, the potential steps from 0V to an oxidative potential of: plot a) 2.0V, plot b) 1.7V and plot c) 1.4V. The legend of each plot shows the individual colour plotted for the diatom distance from the electrode.

Chemical Identification: Chemical Reactions

The all-important question that interests the chemist is; what is the identity of the electro-generated species causing the change in the phytoplankton fluorescence? In this work, the fluorescence response of different phytoplankton species, more of which are shown later, were studied with an applied potential of +2.3V (vs Ag) on a carbon fibre electrode. The f/2 culture medium which the diatom were cultured in contains a large amount of salt – predominantly sodium chloride. At this oxidising potential, the generation of the following species are thermodynamically favourable where their diffusion coefficients are shown in brackets: dichlorine, Cl_2 ($1.38 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$),⁵¹ from oxidation of Cl^- anion, and di-oxygen ($1.9 - 2.1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$),⁵²⁻⁵⁵ hydrogen peroxide ($1.43 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$)⁵⁵ and hydroxyl radicals ($1 - 3 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$)^{56, 57} from hydrolysis of water; all of which have comparable diffusion coefficients. However, due to the lack of adsorption sites for the stabilisation of intermediates on carbon surface (in contrast with platinum surfaces for example) will likely lead to the formation of hydroxyl radicals and hydrogen peroxide from the hydrolysis of water. Likewise, the formation of Cl_2 primary via a Cl^- intermediate is less favourable on the carbon surface as compared to a platinum surface. In order to try and identify the active species, the *in vivo* chl-a fluorescence spectra of *H. coffeaeformis* culture was studied in homogenous solution as a function of the chemical conditions (H^+ , H_2O_2 , Fe^{2+} , OH^-/OOH^- , Cl_2 or OCl^-).

Figure 4.8 shows the fluorescence spectrometer measurements of *H. coffeaeformis* culture (2.5 ml) with the addition of different chemical species (0.5 ml). After the addition and with sufficient mixing, the chl-a emission measurements were taken immediately in the spectrometer sweeping from 750 nm to 630 nm under excitation wavelength of 430 nm; the data acquisition takes approximately 10 s. The timescale allowing the reaction to

occur is not too dissimilar to that seen in the fluoro-electrochemical experiments. As can be seen in Figure 4.8, qualitatively, the chl-a fluorescence emission peak at 680nm did not change significantly with the addition of either 0.5 ml of 0.1 M $\text{HCl}_{(\text{aq})}$, H_2O_2 (33 %) or 100mM $\text{FeSO}_{4(\text{aq})}$. The variations in fluorescence intensity between these experiments most likely reflect the sedimentation of diatoms and the inherent self-protection mechanism of the plankton to strong incident light.

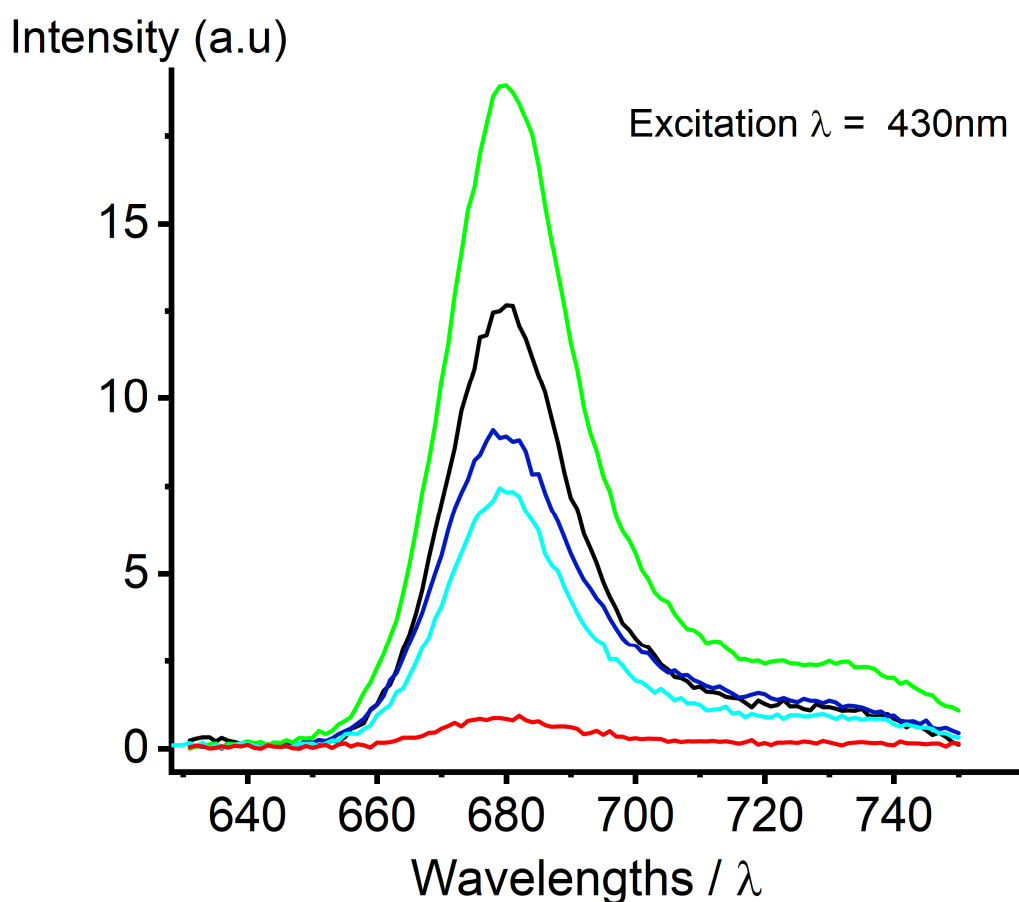


Figure 4.8. Fluorescence spectrometer emission measurements of 2.5ml *H. coffeaeformis* culture with the addition of 0.5ml of: black line – H_2O , blue line - 0.1M HCl , green line – 33% H_2O_2 , turquoise line – 0.1M FeSO_4 and red line – 0.1M FeSO_4 and 33% H_2O_2 (Fenton's reagent).

However, the addition of H_2O_2 (33 %) together with 100 mM $\text{FeSO}_{4(\text{aq})}$, (known as “Fenton's reagent”) led to a significant drop in emission intensity at 680nm. The Fe^{2+} is well known to act as a catalyst for the breakdown of H_2O_2 to in situ generates $\text{OH}^\cdot$ dramatically kills the phytoplankton fluorescence⁵⁸

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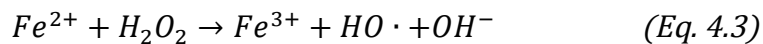


Figure 4.9 shows the fluorescence spectrometer measurements of the *H. coffeaeformis* culture with the addition of NaOCl or chlorine gas. The results show a strong reduction in the fluorescence in the presence of Cl₂ (and NaOCl) similar to that observed with Fenton's reagent. Moreover, Figure 4.10 shows a plot of the fluorescence response time of individual diatoms to the applied potential, verses distance squared, in chloride-containing medium and non-chloride containing medium. At similar distances away from the electrode, the presence of Cl⁻ anion in the solution leads to a faster fluorescence switch off compare to NO₃⁻. This shows that fluorescence susceptibility of *H. coffeaeformis* to the electrode generated species is higher in the chloride-containing medium, which may be due to the formation of chlorine gas. However, as evidenced by Figure 4.10 where the electrochemical inhibition occurs in 0.1 M KNO₃, the presence of chloride is not essential for the fluorescence switch off.

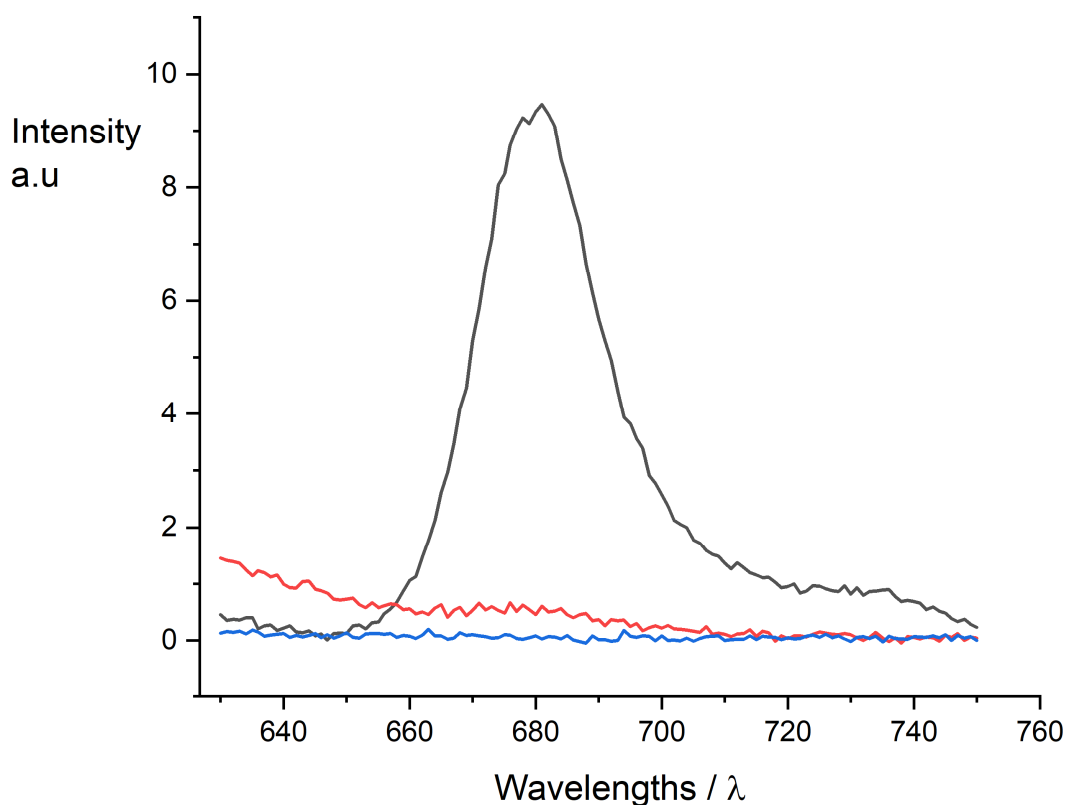


Figure 4.9. Fluorescence spectrometer emission measurements of 2.5ml *H.coffeaeformis* culture with the addition of 0.5ml of: black line – H_2O , red line – $NaOCl$ (1.26g/ml) and blue line – H_2O + chlorine gas.

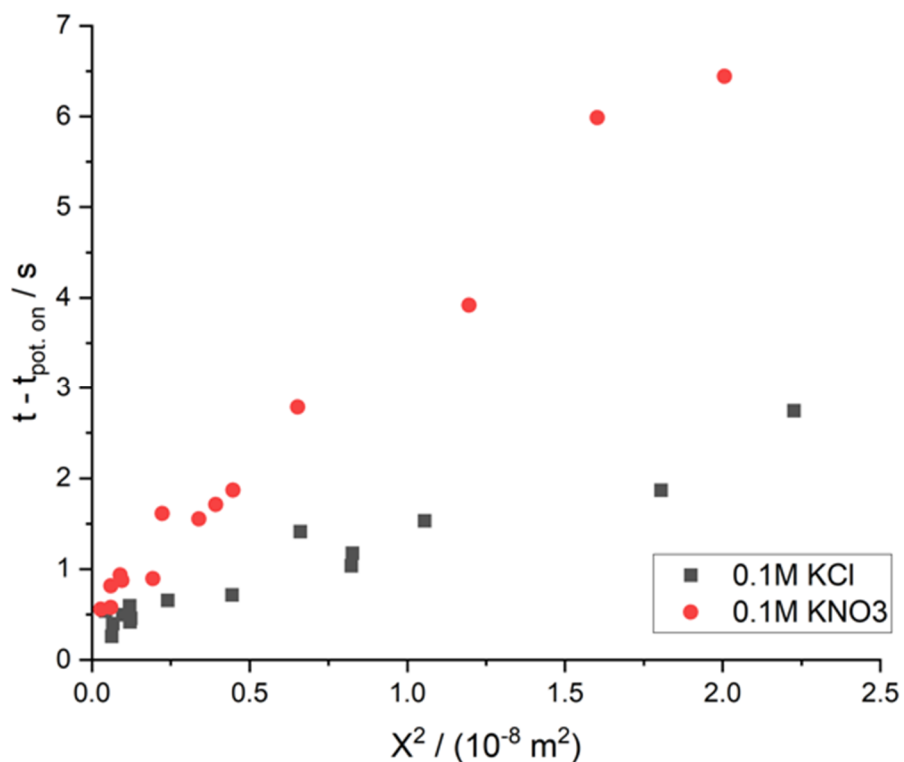


Figure 4.10. The offset time which the fluorescence of individual *H.coffeaeformis* responses to the onset potential of +2.3V (vs Ag) plotted against their distance away from the electrode squared. The *H.coffeaeformis* culture were centrifuged for 1 min at 1000 rpm, and the supernatant was replaced with 0.1M KNO_3 (red circles) or 0.1M KCl (black squares).

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In summary, although chlorine can also lead to the oxidative destruction of the chl-a phytoplankton fluorescence signal, the data provided in Figure 4.10 demonstrates how the electrochemical inhibition may also be driven to occur in the *absence* of solution-phase chloride. As the presence of chloride is not essential, it is therefore likely that oxidative radical species other than chlorine based are the primary cause of the fluorescence inhibition. Furthermore, despite the fact that Fenton's reagent forms hydroxyl radicals, the latter species is highly reactive with a sub-microsecond lifetime.⁵⁶ Consequently, since the phytoplankton are situated away from the electrochemical interface it may be the products indirectly generated from hydroxyl radical reactions²⁹ that propagate away to react with the phytoplankton and are the primary cause of the observed fluorescence 'switch off'. However, the direct involvement of very low OH[•] concentration cannot be discounted and so, in summary, it can be concluded, at present, that OH[•] or products derived from it are responsible for the switch off. Next, we turn to consider how other species of phytoplankton are affected by the electro-oxidation process.

4.3.2 Susceptibility of Phytoplankton Speciation Towards Oxidative Damage

First, the fluoro-electrochemical experiment was conducted with a cell containing 3 phytoplankton species which are distinguishable under the optical setup; the diatom *H. coffeaeformis* (as used above), the coccolithophore *E. huxleyi* and the dinoflagellate *S. trochoidea*. Only one individual dinoflagellate *S. trochoidea* is present in this experiment as the number density of this species, due to its significantly larger cellular size, reaches a maximum of $\sim 10^3$ per ml as compared to the others which can be cultured to 10^6 per ml. Please see the video provided in Additional Materials named 'Phytoplankton – Video Two (.mp4)', a description of which can be found in Section 4.2.6.

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Figure 4.11 shows the fluorescence responses of a representative sample of *E. huxleyi* in presented in Video Two – all show a small rise in fluorescence intensity before rapidly switching off. This rapid decrease in intensity suggests that the plankton outer structure is not initially permeable to the formed radicals but the once that cell wall or membrane has been breached the cell rapidly loses its fluorescence signal. Note if the different behaviour was due to slow mass-transport through the cells internal structure or due to low permeability of the radical species across the interface one would expect the intensity/time transients to be markedly different - in this case one would expect a slower and monotonic decrease in the phytoplankton fluorescence response. The results in Figure 4.11 likely indicate that the microalgal cell wall or membrane is chemically attacked by the formed radical species leading to a catastrophic and rapid loss of integrity.

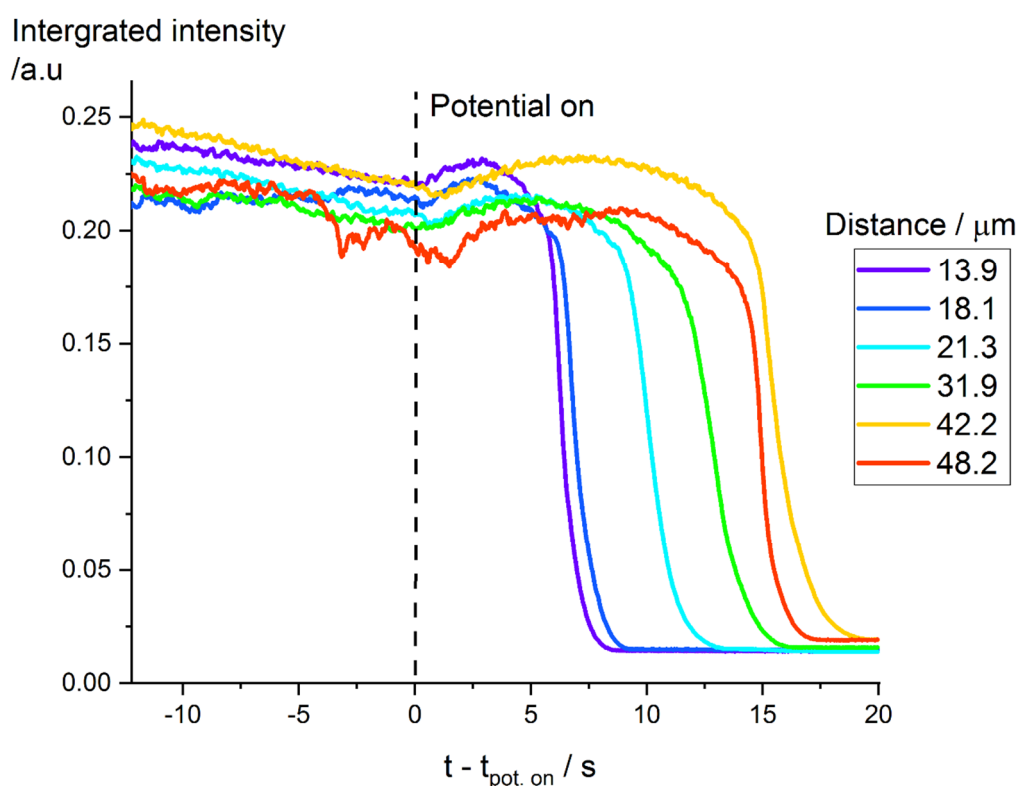


Figure 4.11 Normalised fluorescence intensity of individual *E. Huxleyi* located at different distances from the electrode during the fluoro-chronoamperometry experiment (video of which can be found as *Phytoplankton-Video Two.mp4* in 'Additional Materials'). At time of 60 seconds a potential of +2.3V (vs Ag pseudo wire) is applied to the electrode.

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At this point, one may ask how does the rate of this chl-a switch off (for coccolithophore *E. huxleyi*) compare to that seen for diatom *H. coffeaeformis*; which is more resilient towards oxidative damage? Figure 4.12 shows a plot of the normalised fluorescence intensity, for a representative individual *H. coffeaeformis* and *E. huxleyi*, approximately equidistant from the electrode (ca. 20 μm), plotted against time after the onset of the oxidising potential. First, the *H. coffeaeformis* fluorescence (yellow line) starts to decrease only a second after the electrode potential has been switched to +2.3 V. Second, in contrast, the fluorescence intensity of the *E. huxleyi* (red line) initially increases slightly but then shows a dramatic decrease in fluorescence intensity *after 15 s* of electrode potential being changed.

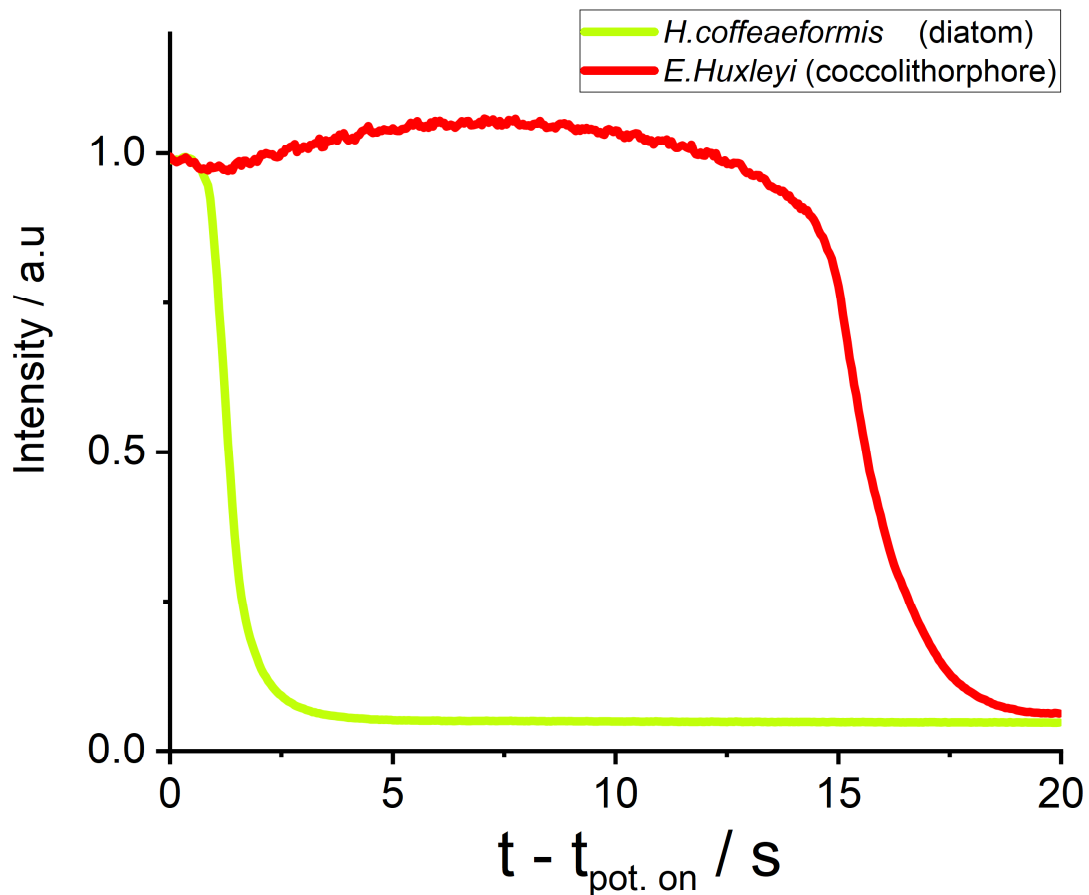


Figure 4.12 Chlorophyll-a fluorescence response of diatom (*H. coffeaeformis*, CCAP 1001/2, yellow line) and coccolithophore (*E. huxleyi*, RCC 174, red line) at equal distance $20 \pm 1 \mu\text{m}$ away from the electrode. Data extracted from *Phytoplankton-Video Two.mp4* in 'Additional Materials'.

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As shown in Figure 4.11 this rapid drop in fluorescence intensity is a general feature of the *E. huxleyi* response towards the oxidative conditions. These two plankton are present in the *same* electrochemical experiment, and hence the differing behaviour is not related to any variability in the electrochemical conditions. The rapid loss of fluorescence for the *E. huxleyi* after an initial delay most likely arises due to the cells outer structure being initially less permeable to the oxidative species followed by the sudden and rapid breaching of the shell, presumably caused by external chemical attack of the oxidative radical species. This conclusion is corroborated by the recorded microscope response of the *S. trochoidea*, this phytoplankton is relatively large compared to the others used in this study with a diameter of $>20\text{ }\mu\text{m}$. Consequently, with the use of a 40X objective lense the internal structure of the plankton can be monitored; the experimental video (please see ‘Phytoplankton – Video Three.mp4’ in Additional Materials) shows that the major decrease in the phytoplankton fluorescence occurs after an abrupt change in the phytoplankton structure; which is likely associated with the rupturing of the cells external protection layer. These results are strongly suggestive that difference in the behaviour of the species relates not to their size but due to their differing biomineral covering or outer membrane structures.

So far, the above has reported that the susceptibility towards oxidative ‘attack’ is drastically altered between two very different phytoplankton species, siliceous-shelled diatom *H. coffeaeformis* and calcifying coccoplithophore *E. huxleyi*; the questions arises as to what happens for a wider range of plankton species? The fluoro-electrochemical experiment described above was undertaken with an additional four different species of phytoplankton. Figure 4.13 a) plots the total collated results for the seven different phytoplankton species studied, here the onset of the fluorescence decrease as a function

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of time has been plotted against the square of the phytoplankton distance from the electrode. Figure 4.13 a) shows that, although for a given species there is a strong correlation between the distance between the electrode and the time at which the fluorescence inhibition onsets, there is a very wide difference in behaviour between the different species. For example, on the time scale of this experiment, only ca. 24% of the *E. huxleyi* observed within the field of the microscope were affected by the oxidative potential and all of those affected were within 60 μm of the electrode. In contrast, the fluorescence signals of all of the *S. bacillaris*, within a distance of approximately 100 μm of the electrode, were inhibited within 2 seconds of the oxidising potential being applied to the electrode. Note, the dinoflagellate *S. trochoidea* was also studied within the electrofluorescence cell. *S. trochoidea* are relatively large and present in solution at low cell densities. Hence, the imaging of only three individual *S. trochoidea* was achieved the results of which are presented in Figure 4.13 a) black squares. For all of the species presented in Figure 4.13 a) – excluding *S. trochoidea*, for which insufficient data could be acquired – the scatter plot for each species is quasi-linear; the 95% confidence interval of a line of best fit is overlaid on the data.

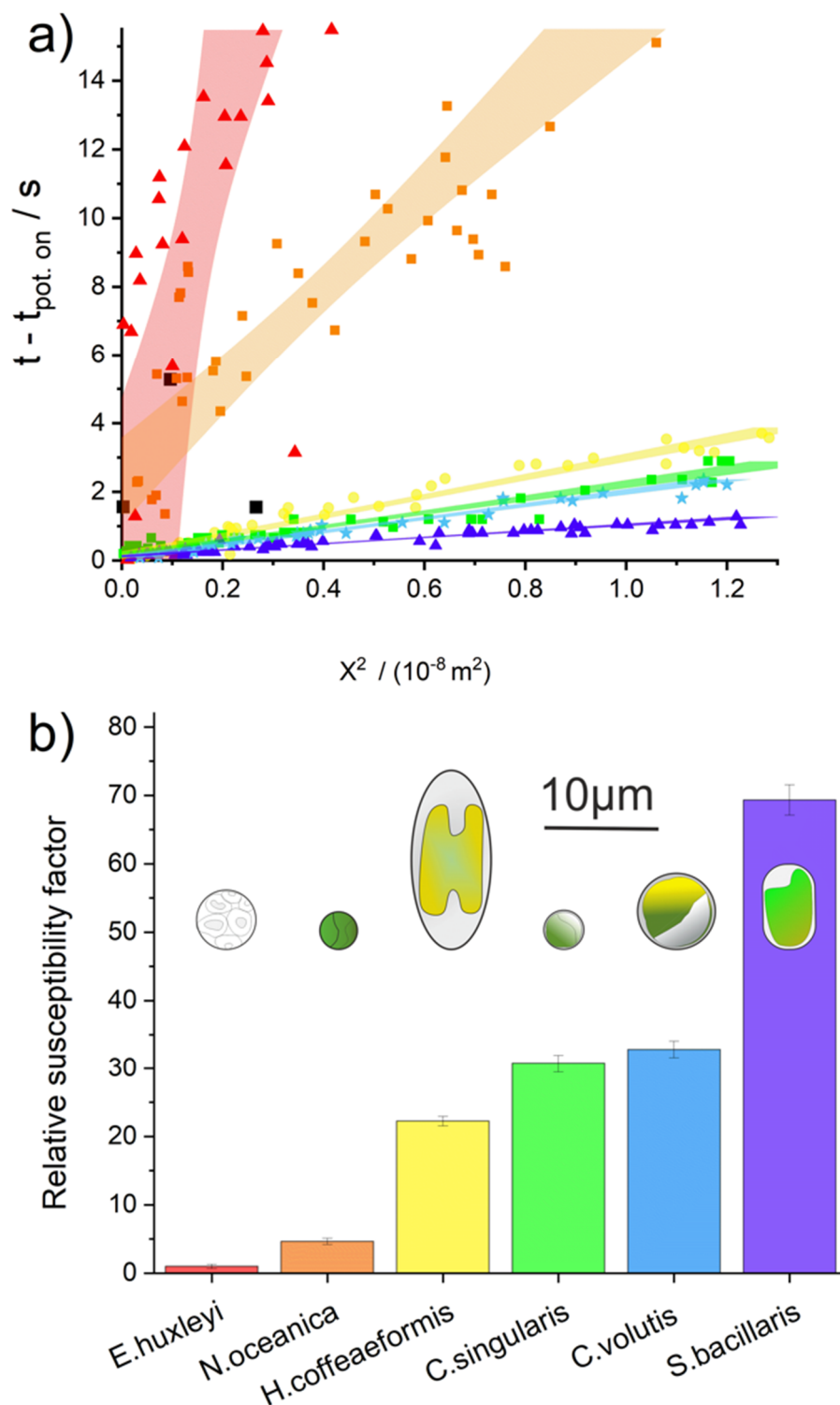


Figure 4.13. a) A plot of time at which chl-a fluorescence decrease abnormally after application of an oxidising electrode potential versus square of the distance of the phytoplankton from the electrode. Red triangles – *E. huxleyi*; orange squares – *N. oceanica*; yellow circles – *H. coffeaeformis*; green squares – *C. singularis*; blue stars – *C. volutis*; magenta triangles – *S. bacillaris* and black squares – *S. trochoidea*. The highlighted areas depict the 95% confidence for the line of best fit as used in the calculation of the susceptibility factor, note the line of best fit has not been forced through the origin. b) plots the relative susceptibility factor for each species towards oxidative radical attack, normalised to *E. huxleyi*. Also shown on this plot are cartoons representing the size and shape of the plankton involved, this demonstrates that there is no clear correlation between the plankton susceptibility and its morphology or size.

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This linearity in the plot of the square of the distance versus time predominantly reflects the fact that the reactive species created at the electrode need to diffuse away from the interface prior to reacting with and damaging the phytoplankton. For a molecule freely diffusing in solution, the mean square distance travelled $\langle X^2 \rangle$ in one dimension is equal to:⁵⁹

$$\langle X^2 \rangle \approx 2Dt \quad (\text{Eq. 4.5})$$

where D ($\text{m}^2 \text{s}^{-1}$) is the diffusion coefficient and t is time (s). Consequently, after ten seconds, a molecule with a diffusion coefficient of $1 \times 10^{-9} \text{ m}^2 \text{s}^{-1}$ will have travelled on average a distance of $\sim 140 \text{ }\mu\text{m}$. Such distances are comparable to those we observe optically. In Figure 4.13 a) and using the relationship shown in Equation 4.5, the inverse of the gradient of the line of best fit can be used to characterise the rate at which the phytoplankton respond to the oxidative potential on the electrode. This inverse gradient is termed the ‘susceptibility factor’ and it reflects the rate of mass-transport of the radical species, the used experimental conditions and the susceptibility of the plankton species towards attack from the oxidative radicals. Appendix: A presents a simple theoretical model exploring the dependency of the response time on the diffusional mass-transport rate and phytoplankton susceptibility and gives physical insight into the underlying processes. Ultimately, as the fluorescence response of the plankton are recorded under the same experimental conditions, the measured t vs X^2 gradient for the different plankton can be used to give a relative measure of their susceptibility to strongly oxidising environments. Figure 4.13 b) presents the plot of the relative susceptibility factor for the different phytoplankton, normalised against the measured rate for the phytoplankton most resilient to oxidative environment in this study, *E. huxleyi*. These experimental values differ by almost two orders of magnitude, such that, the least resilient and hence plankton

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with the highest susceptibility, freshwater algae *S. bacillaris* reacts 69 ± 2 times faster than the calcifying coccolithophore *E. huxleyi*.

It is noteworthy that first, the data presented in Figure 4.13 b) does not reflect either the size or shape of the phytoplankton. Overlaid on Figure 4.13 b) are schematic diagrams that show the approximate size and morphology of the used phytoplankton species, the diatom *H. coffeaeformis* is the largest phytoplankton for which a relative susceptibility factor has been measured; however, its value is similar in magnitude to significantly smaller plankton. Moreover, the plankton *C. singularis* and *C. volutis*, are of the same genus and have very comparable relative susceptibility factors, but they are distinctly different in size. Second, broadly the freshwater species (*C. singularis*, *C. volutis* and *S. bacillaris*) appear to be more susceptible to oxidative attack than the marine species (*E. huxleyi*, *S. trochoidea*, *N. oceanica* and *H. coffeaeformis*). These results further corroborate the conclusion that the difference in the observed fluorescence behaviour predominantly reflects the chemical and physical characteristics of the phytoplankton shell and outer membranes. Consequently, the susceptibility of the phytoplankton towards oxidative radical attack is evidenced to be group-specific and reflects the diverse structural properties of the exterior of these microscopic single-cell organisms.

Moreover, recent work by a Masters student in the group (Ms Junling Ma) investigated the susceptibility of artificially synthesised ‘phytoplankton’, chl-a containing oil-in-water emulsion, stabilised by a molecular layer of surfactant (sodium dodecyl sulfate, SDS). The unpublished work shows an excellent agreement to that reported above for freshwater algae *S. bacillaris*. One may infer that this species of freshwater algae have little to no resistance towards oxidative damage and the rate of which is diffusional controlled as can

be deduced by the minimal protection provided by the nanoscopic, biomimicking layer of SDS as the cellular wall.

4.4 Conclusions

In this work, the chl-a fluorescence of phytoplankton was investigated using a fluoro-electrochemical cell. The phytoplankton were found to be highly sensitive to electrochemically oxidising environment. The *in situ* electrochemically generated radical species irreversibly kill the phytoplankton fluorescence. This inhibition rate is evidenced to reflect neither the size nor the shape of the phytoplankton but most likely relates to the physical and chemical properties of the shell and outer membrane of the phytoplankton; the rate-determining step is the chemical destruction of the outer cellular structure, once the radicals enter the cell the chl-a fluorescence is rapidly extinguished. Profoundly, the rate at which the fluorescence is inhibited varies between species by almost two orders of magnitude. Beyond, possible biological implications of the differing susceptibility of different plankton group towards extreme oxidative stress, on a pragmatic level the ability to differentiate between phytoplankton on the basis of their oxidative susceptibility has potential application in high-throughput methods for phytoplankton identification and bloom monitoring.

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Chapter 5 An Introduction to Electrochemical Simulation: Numerical Methods

The mathematics behind electrochemical systems, when more than one electrochemical reaction are involved, typically escalates in their complexity in which analytical expressions become underivable.^{1, 2} The electrochemical reactions may include multiple electron-transfer steps, follow-up chemical reactions and/or surface adsorption etc.^{3, 4} One should not, however, be ‘beaten’ when facing an electrochemical system with complex and analytically unsolvable mathematics, as meaningful insights can be obtained from a numerical simulation. In this Chapter, the numerical methods discussed herein will allow one to understand the mathematical approach to numerically simulating a simple one-electron transfer reaction $A(aq) + e^- \rightleftharpoons B(aq)$; extension to simulating *any* complex electrochemical systems of interest is often entirely possible. The discussions here follows from the fundamental electrochemistry introduced in Chapter 1.

As a side note, although there are numerous commercially available electrochemical simulation packages, examples are Digisim, COMSOL and DigiElch etc. These softwares are optimised in performance, allow multiple-electron transfer reactions, homogeneous chemical reactions on various (predominantly 1-D) electrode geometries to be simulated. The simulation results obtained from such ‘black boxes’ are, however, unsatisfactory since the calculations performed are not transparent to the user. Moreover, the optimised performance may be somewhat compromised for numerical convergence. This could result in numerical instability, especially when extreme values of physical parameters are used. It is partly because of this reason, the purists of all turns seek to develop their bespoke simulation programs, first, tailoring to their electrochemical

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system of interest – with may require features not part of the commercially available software – and second, the user retains *complete control* of the numerical calculations and numerical transparency at all times.

The Chapter begins with a simple overview of the mathematics involved in formulating a simple electrochemical system, $A(aq) + e^- \rightleftharpoons B(aq)$. Then the discussion will move on to how partial differential equations can be approximated with *only* basic mathematical operations (+, -, * and /) which can be interpreted by the computer. At the end of the Chapter, a multidimensional root finding method, named after Issac Newton and Joseph Raphson, is introduced. This method is required to solve the non-linear simultaneous equations of more complex electrochemical models, later presented in Chapter 6 and 7.

The mathematics introduced herein can be written and implemented in any suitable programming language of preference. Examples include C++, C, Python, Matlab and Fortran etc. To develop the simulation models the author learnt all the necessary knowledge to code in C++ from a free and well-structured C++ tutorial website, which is exceptionally good for both beginners and advance programmers (www.learncpp.com).

5.1 Mathematical Formulation

In the electrochemical systems discussed herein, the chemical composition of the electrochemical cell is initially homogeneous and the bulk concentration is known before the experiment. In real life, this is easily achievable as chemical solutions can be prepared with high precisions in measurement, and thorough mixing is, of course, second nature to Chemists.

For macro-electrodes, as discussed in Chapter 1, the edge effects are negligible in comparison to the geometric area of the electrode. Therefore the changes in concentration profile in the aqueous phase can be considered as one-dimensional distance, x , perpendicular from the surface of the electrode.

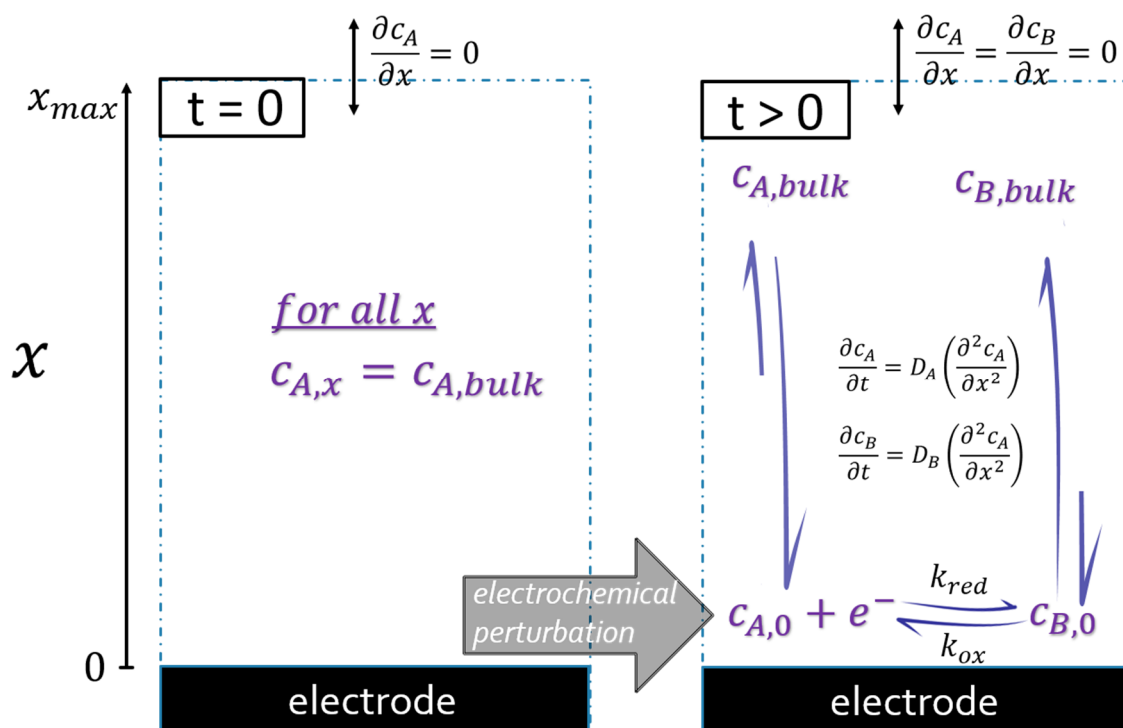


Figure 5.1. An illustration of the physicochemical processes involved in an electrochemical experiment. where x_{max} is a distance (m) defined well beyond the Nernst diffusion layer thickness, t is time (s), and D_A and D_B are the diffusion coefficients (m^2s^{-1}) for species A and B, respectively.

The physicochemical processes formulating the mathematics in an electrochemical experiment are shown in Figure 5.1. At $t = 0$, the concentration is homogeneous in the

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solution phase and $c_{A,x}$ equals to $c_{A,bulk}$ for all x . At $t > 0$, the interfacial redox reaction is driven by the potential waveform of choice, the electrode kinetics can be described by the Butler-Volmer kinetics (Section 1.2) or other appropriate kinetics such the Nernst equation or the Marcus-Hush model.² As reactants are consumed and products are formed at the electrode interface, differences in concentration to the bulk values are developed. This results in concurrent mass transport of materials *down* the concentration gradient. In the presence of sufficient inert supporting electrolyte and in the absence of forced convection, the temporal evolution of concentration is described by Fick's second law (Section 1.3).

The next section introduces the finite difference methods, which approximates the partial differential equation as a series of elementary operations (+, -, * and /).

5.2 The Finite Difference Method

In the finite difference method, the continuous partial differential equations are represented by a series of finite steps, which in turn, can be expressed as a series of elementary operations (+, -, * and /) which are computational operatable. An example of particular relevance is the concentration profile of the redox species, reactant c_A and product c_B , during the electrochemical experiment. As suggested in Figure 5.1 and as can be inferred from Fick's second law, concentration is a function of both time (t) and distance from the electrode (x). First, as a starting point, the spatial discretisation of c_A at an instantaneous time is discussed. Then the focus turns to discuss the temporal and spatial discretisation of c_A .

5.2.1 Spatial Coordinates

First-Order Derivative: Two-Point Approximation

In this subsection, the concentration profile c_A at an *instantaneous time* is considered. Figure 5.2 shows two identical concentration profiles, one as a continuous function of distance x from the electrode, and the other describes the concentration profile as a series of discrete spatial coordinates. The spatial coordinates expand from the electrode surface ($x = 0$) to a distance much beyond the Nernst diffusion layer thickness x_{max} . The expansion can be either uniformly spaced or non-linearly spaced. The mathematics discussed here remains general and it can be applied to all spatial grids regardless of the spacing patterns.

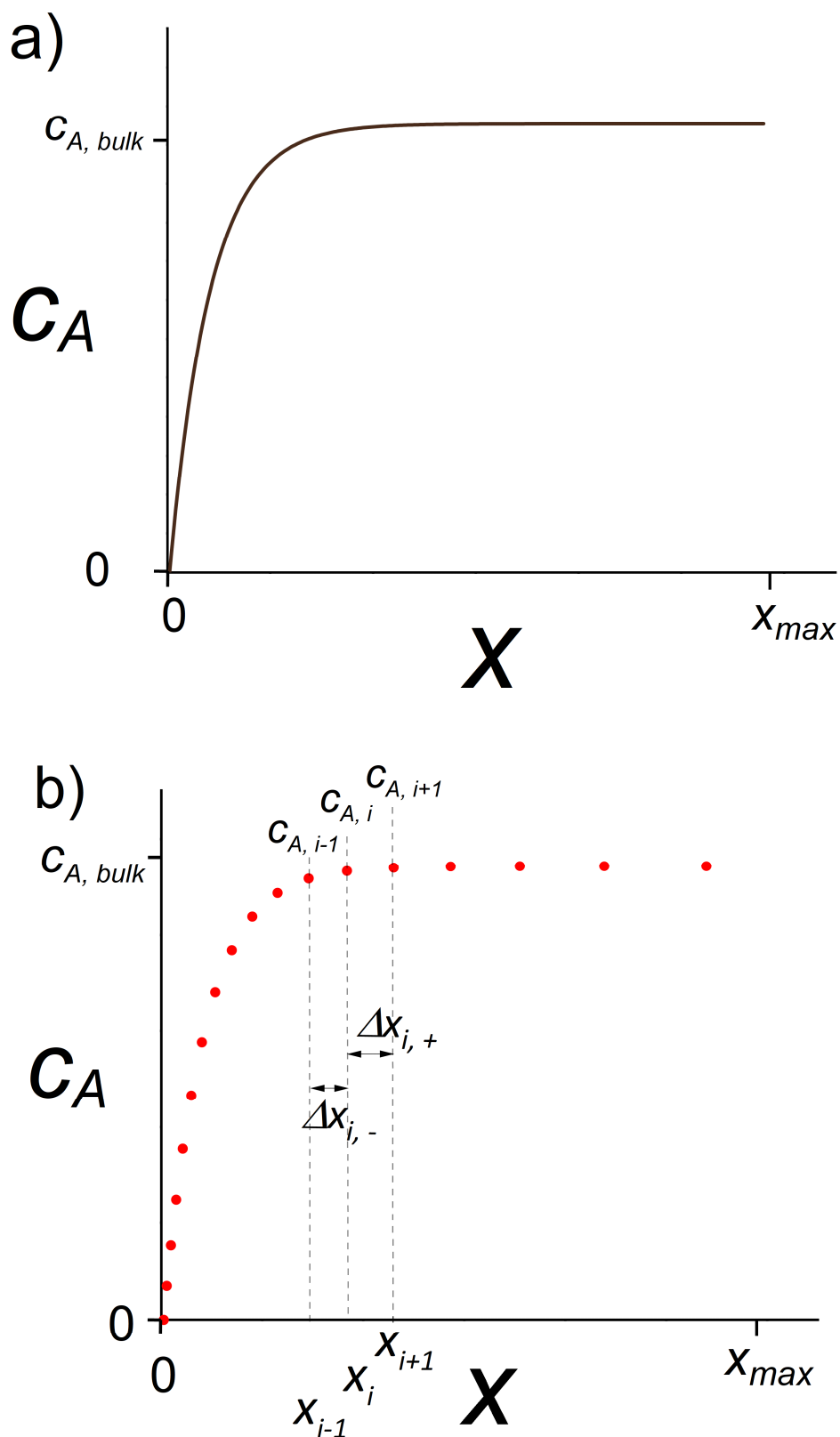


Figure 5.2. a) continuous variation of concentration $c_{A,x}$ as a function of distance x away from the electrode surface. b) concentration profile $c_{A,x}$ represented in a discretised spatial grid. The concentration between the adjacent points is assumed linear.

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To a good approximation, the first derivative of concentration $\frac{dc_A}{dx}$ can be approximated as the concentration gradient between the adjacent discretised spatial points:

$$\left(\frac{dc_A}{dx}\right)_{x_i, \text{ forward}} \approx \frac{c_{A,i+1} - c_{A,i}}{\Delta x_{i,+}} \quad \& \quad \left(\frac{dc_A}{dx}\right)_{x_i, \text{ backward}} \approx \frac{c_{A,i} - c_{A,i-1}}{\Delta x_{i,-}} \quad (\text{Eq. 5.1})$$

where $\Delta x_{i,+} = x_{i+1} - x_i$ and $\Delta x_{i,-} = x_i - x_{i-1}$, the notation i denotes the index of the spatial coordinates, as illustrated in Figure 5.2 b). Note that, for a uniformly discretised spatial grid, $\Delta x_{\text{forward}} = \Delta x_{\text{backward}} = \Delta x$.

The truncation error τ introduced by the simple two-point approximation, the *forward* and *backward difference*, can be found by Taylor series expansion of the concentration

$$c_{A,i+1} = c_{A,i} + \Delta x_{i,+} \left(\frac{dc_A}{dx}\right)_{x_i} + \frac{(\Delta x_{i,+})^2}{2} \left(\frac{d^2c_A}{dx^2}\right)_{x_i} + \left[\dots (\Delta x_{i,+})^3 + \dots \right] \quad (\text{Eq. 5.2})$$

$$c_{A,i-1} = c_{A,i} - \Delta x_{i,-} \left(\frac{dc_A}{dx}\right)_{x_i} + \frac{(\Delta x_{i,-})^2}{2} \left(\frac{d^2c_A}{dx^2}\right)_{x_i} - \left[\dots (\Delta x_{i,-})^3 + \dots \right] \quad (\text{Eq. 5.3})$$

where the terms in the square bracket denote the higher-order terms containing Δx , which becomes increasingly negligible as Δx is typically small. Rearranging for the first derivative of concentration gives

$$\left(\frac{dc_A}{dx}\right)_{x_i, \text{ forward}} = \frac{c_{A,i+1} - c_{A,i}}{\Delta x_{i,+}} - \frac{\Delta x_{i,+}}{2} \left(\frac{d^2c_A}{dx^2}\right)_{x_i} - \left[\dots (\Delta x_{i,+})^2 + \dots \right] \quad (\text{Eq. 5.4})$$

$$\left(\frac{dc_A}{dx}\right)_{x_i, \text{ backward}} = \frac{c_{A,i} - c_{A,i-1}}{\Delta x_{i,-}} + \frac{\Delta x_{i,-}}{2} \left(\frac{d^2c_A}{dx^2}\right)_{x_i} - \left[\dots (\Delta x_{i,-})^2 + \dots \right] \quad (\text{Eq. 5.5})$$

On close inspection between Equations 5.1, 5.4 and 5.5, one can see that the leading-order term in the truncation error (τ) is linearly proportional to $\Delta x_{i,+}$ (or $\Delta x_{i,-}$).

First-Order Derivative: Central Difference Approximation

Considering the *forward* and *backward* two-points approximation as introduced above; a better estimate can be obtained by averaging the above two-point *forward* and *backward* approximations. This is known as the *central difference approximation*

$$\begin{aligned} \left(\frac{dc_A}{dx}\right)_{x_{i,central}} &= \frac{1}{2} \left[\left(\frac{dc_A}{dx}\right)_{x_{i,forward}} + \left(\frac{dc_A}{dx}\right)_{x_{i,backward}} \right] \\ &\approx \frac{1}{2} \left[\frac{c_{A,i+1} - c_{A,i}}{\Delta x_{i,+}} + \frac{c_{A,i} - c_{A,i-1}}{\Delta x_{i,-}} \right] \end{aligned} \quad (Eq. 5.6)$$

This approximates the concentration gradient around $c_{A,i}$ by involving two of its adjacent spatial points and itself, $c_{A,i+1}$, $c_{A,i}$ and $c_{A,i-1}$, as can be seen in Figure 5.2 b). This approximation is more accurate because the leading-order terms in the two-point truncation error (Γ) approximately cancel out

$$\Gamma_{central} = \frac{[\Gamma_{forward} + \Gamma_{backward}]}{2} = \frac{1}{4} [\Delta x_{i,-} - \Delta x_{i,+}] \left(\frac{d^2 c_A}{dx^2}\right)_{x_i} - \frac{[\dots(\Delta x_{i,+})^2 + \dots(\Delta x_{i,-})^2 + \dots]}{2} \quad (Eq. 5.7)$$

Note that, the first term on the right-hand side of Equation 5.7 is exactly zero in the case of a uniformly discretised spatial grid, where $\Delta x_{i,-} = \Delta x_{i,+} = \Delta x$. This is approximately the case for an expanding grid, providing the expansion factor is sufficiently small such that $\Delta x_{i,-} - \Delta x_{i,+} \approx 0$. Thus, the truncation error introduced in the three-point approximation is much smaller than that of the two-point equivalent. Thus three-point approximation is used herein to improve the accuracy without adding too much complexity.

Second-Order Derivative

The second-order derivative of concentration c_A with respect to x is part of Fick's second law of diffusion, necessary to account for the mass transport to and from the electrode. The second-order derivative can be approximated from the first-order discretisation

$$\left(\frac{d^2 c_A}{dx^2}\right)_{x_i} = \frac{\partial}{\partial x} \left(\frac{dc_A}{dx}\right)_{x_i} \approx \frac{\left(\frac{dc_A}{dx}\right)_{x_{i,forward}} - \left(\frac{dc_A}{dx}\right)_{x_{i,backward}}}{\frac{1}{2}(\Delta x_{i,+} + \Delta x_{i,-})} \quad (Eq. 5.8)$$

Substituting Equation 5.4 and 5.5 into the above equation gives

$$\left(\frac{d^2 c_A}{dx^2}\right)_{x_i} \approx \frac{\frac{c_{A,i+1} - c_{A,i}}{\Delta x_{i,+}} - \frac{c_{A,i} - c_{A,i-1}}{\Delta x_{i,-}}}{\frac{1}{2}(\Delta x_{i,+} + \Delta x_{i,-})} \quad (Eq. 5.9)$$

So far, the second derivative of concentration is treated with one independent variable, distance from the electrode x , as if ‘frozen’ at an instantaneous time t . But, Fick’s second law of diffusion states that the concentration is also a function of time t . In the next section, the methods to discretise Fick’s second law of diffusion in *both* the spatial and temporal domain are discussed.

5.2.2 Temporal Coordinate: Explicit and Implicit Methods

The concentration is not only a function of distance x , but also a function of time t as described by Fick’s second law of diffusion (Section 1.3). The two methods discussed herein are named the explicit and backwards-implicit method, differ in their temporal discretisation in calculating for the unknown concentration in question, $c_A(x, t)$. Figure 5.3 is a schematic illustrating their differences. The square represents the unknown concentration one wish to calculate at the present timestep, and the circles are the data required for such numerical calculation.

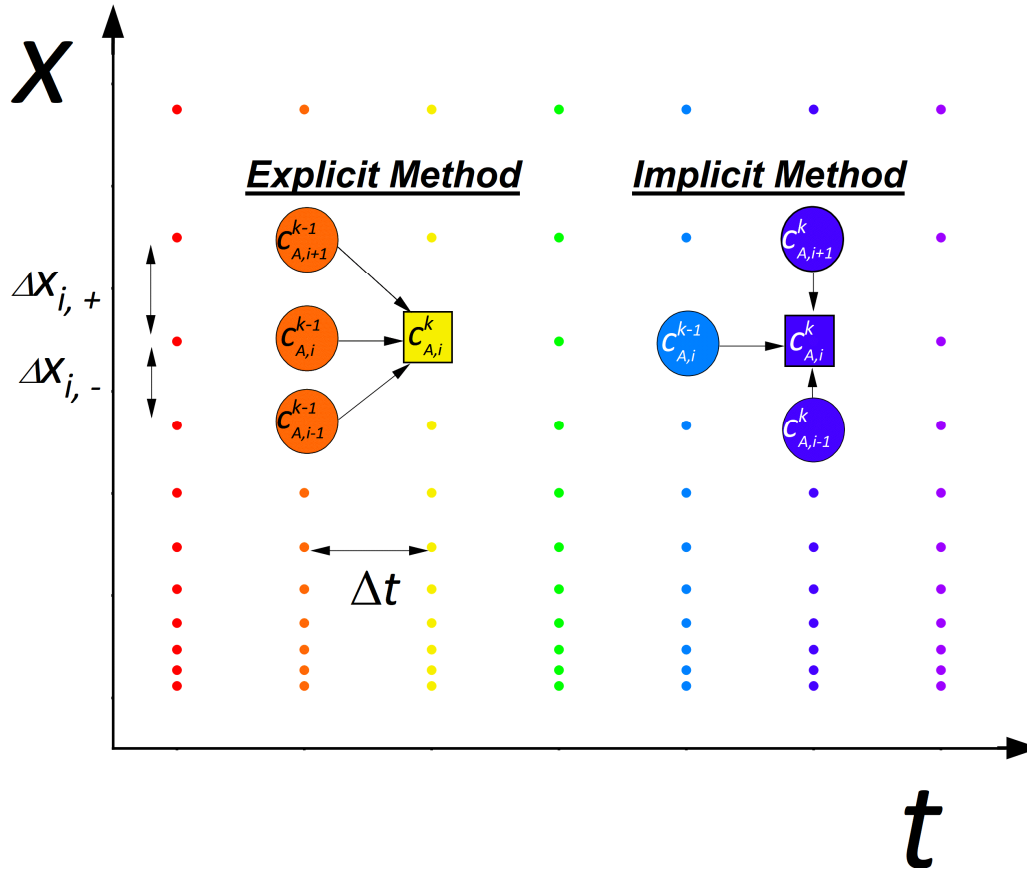


Figure 5.3. Illustration of the explicit and backward implicit finite difference method, where the x-y axis represents the temporal and spatial grids, respectively. The circles represent the values required to compute the value represented by the square.

The first and more straightforward method is the explicit method, which discretises the temporal domain as follows

$$\frac{c_{A,i}^k - c_{A,i}^{k-1}}{\Delta t} = D_A \frac{\frac{c_{A,i+1}^{k-1} - c_{A,i}^{k-1}}{\Delta x_{i,+}} - \frac{c_{A,i}^{k-1} - c_{A,i-1}^{k-1}}{\Delta x_{i,-}}}{\frac{1}{2}(\Delta x_{i,+} + \Delta x_{i,-})} \quad (\text{Eq. 5.10})$$

where the notation k denotes the discretised temporal points. Here $c_{A,i}^k$ represents the *unknown* concentration of A we wish to compute at a current timestep, whereas all the terms involving temporal coordinate $(k - 1)$ are known from the previous timestep. Thus this can be rearranged to separate the known from the unknowns

$$C_{A,i}^k = C_{A,i}^{k-1} + D_A \Delta t \frac{\frac{C_{A,i+1}^{k-1} - C_{A,i}^{k-1}}{\Delta x_{i,+}} - \frac{C_{A,i}^{k-1} - C_{A,i-1}^{k-1}}{\Delta x_{i,-}}}{\frac{1}{2}(\Delta x_{i,+} + \Delta x_{i,-})} \quad (\text{Eq. 5.11})$$

As can be seen, solving the explicit equation is straightforward as there's only one unknown in the equation, $C_{A,i}^k$. Therefore, the unknowns concentrations spanning over the entire spatial domain, at each timestep, are independent and can be calculated independently. Although straightforward, it is, however, subject to numerical stability. Numerical stability is only achieved when^{5, 6}

$$\lambda \approx \frac{D_A \Delta t}{\Delta x_i^2} < 0.5 \quad (\text{Eq. 5.12})$$

This stability criterion severely limits the potential of this method in solving electrochemical problems. This is because the computational time is inversely proportional to the size of the timestep Δt , meaning a small improvement in the spatial resolution (smaller Δx_i) will cause an exponential increase in computational time, to maintain numerical stability.

The second and more advanced method, introduced in more detail in the next section, is the preferred method and used in the remainder of discussions involving simulation in this thesis. The reason is because it is *not* constrained to the above numerical stability and thus excels in simulation performance, albeit the downside is the increase in complexity.

5.2.3 The Backward-Implicit Method

The temporal discretisation of the backwards-implicit method is different from that of the explicit method (Equation 5.10):

$$\frac{C_{A,i}^k - C_{A,i}^{k-1}}{\Delta t} = D_A \frac{\frac{C_{A,i+1}^k - C_{A,i}^k}{\Delta x_{i,+}} - \frac{C_{A,i}^k - C_{A,i-1}^k}{\Delta x_{i,-}}}{\frac{1}{2}(\Delta x_{i,+} + \Delta x_{i,-})} \quad (\text{Eq. 5.13})$$

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Taking a closer look, one finds that the temporal coordinate on the right-hand side of the equation is the present timestep k , in contrast to $k - 1$ in the explicit method. The question to pose is, how can one solve for $c_{A,i}^k$, when the knowledge of two additional unknowns, namely the adjacent concentration $c_{A,i-1}^k$ and $c_{A,i+1}^k$ are required. First, we rearrange Equation 5.13 to separate the known ($k - 1$) and unknowns (k), this leads to

$$c_{A,i}^{k-1} = \alpha_i c_{A,i-1}^k + \beta_i c_{A,i}^k + \gamma_i c_{A,i+1}^k \quad (\text{Eq. 5.14})$$

$$\text{where } \alpha_{A,i} = \frac{-2D_A\Delta t}{(\Delta x_{i,-}^2 + \Delta x_{i,+}\Delta x_{i,-})}, \quad \beta_{A,i} = 1 + \frac{2D_A\Delta t}{\Delta x_{i,+}^2 + \Delta x_{i,+}\Delta x_{i,-}} + \frac{2D_A\Delta t}{\Delta x_{i,-}^2 + \Delta x_{i,+}\Delta x_{i,-}}$$

$$\text{and } \gamma_{A,i} = \frac{-2D_A\Delta t}{(\Delta x_{i,+}^2 + \Delta x_{i,+}\Delta x_{i,-})}$$

Here the values $\alpha_{A,i}$, $\beta_{A,i}$ and $\gamma_{A,i}$ depend on the expanding grid and the diffusion coefficient of the species of interest, D_A , which are constants and are set at run-time.

Let us take a ‘bird’s-eye view’ of the mathematical problem as a whole. The spatial discretisation starts from the electrode interface, x_0 , and ends to a distance much beyond the Nernst diffusion layer thickness, x_{max} , where the concentration is unperturbed from its bulk value during the timescale of the simulation. At x_0 and x_{max} , there is an associated boundary condition (more of which is discussed in Chapter 6 and 7). For every spatial coordinate i in between the boundary conditions, $x_0 < x_i < x_{max}$, there is an associated implicit equation (5.14) to be solved at each timestep, illustrated in Figure 5.4.

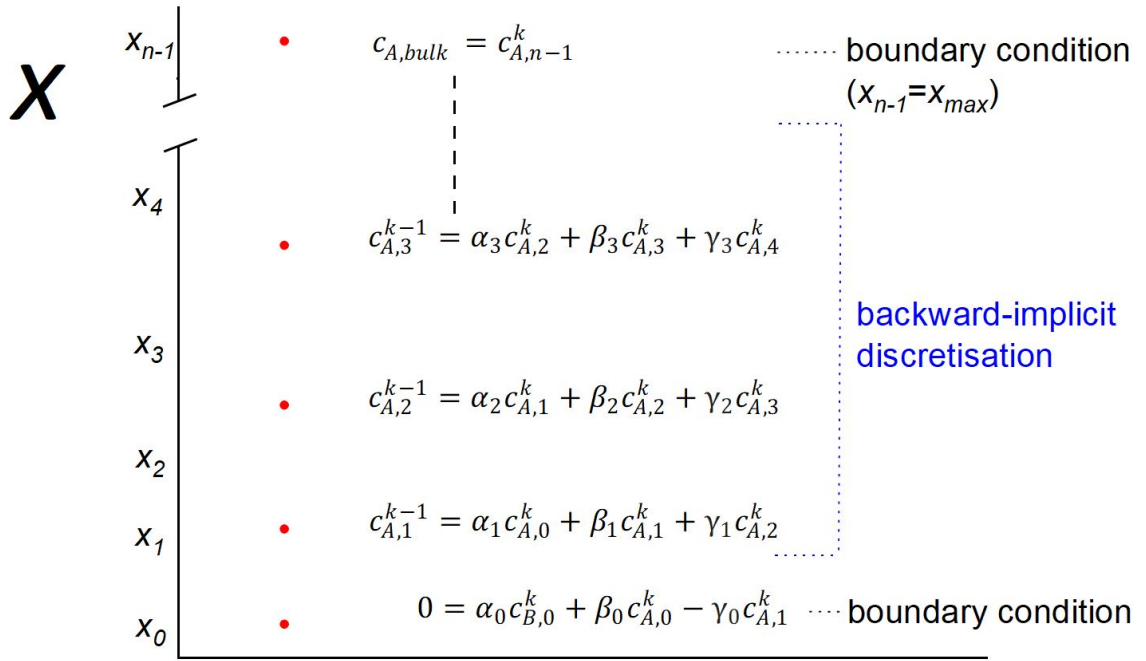


Figure 5.4 Linear algebra for each of the backward implicitly discretised spatial coordinates.

It now becomes clear that, a set of equations has to be solved simultaneously at each timestep. While the solving method, introduced separately in the next section, is mathematically more complicated than that of the explicit method (and involves significantly more lines of code), it is, however, more efficient because it is *not* subject to the numerical stability imposed on the explicit method.² Modern CPUs are extremely efficient in solving large sets of simultaneous equations and in terms of simulation performance, this completely outshines the need to deploy a mind-bogglingly dense temporal grid to maintain numerical stability.

5.3 LU Decomposition: the Thomas Algorithm

The series of linear simultaneous equations obtained from the backwards-implicit method can be generalised for both species involved in the redox reaction A and B with their corresponding diffusion coefficients D_A and D_B . Together, the series of simultaneous equations to be solved can be structured into a *tridiagonal matrix equation* ($\mathbf{Ax} = \mathbf{d}$).

$$\underbrace{\begin{pmatrix} \beta_{A,n-1}\alpha_{A,n-1} & 0 & \cdots & & & & & & \\ \gamma_{A,n-2}\beta_{A,n-2}\alpha_{A,n-2} & 0 & \cdots & & & & & & \\ & \ddots & \ddots & \ddots & & & & & \\ \cdots & 0 & \gamma_{A,1} & \beta_{A,1}\alpha_{A,1} & 0 & 0 & 0 & 0 & \cdots \\ \cdots & 0 & 0 & \gamma_{A,0}\beta_{A,0}\alpha_{A,0} & 0 & 0 & 0 & 0 & \cdots \\ \cdots & 0 & 0 & 0 & \alpha_{B,0}\beta_{B,0}\gamma_{B,0} & 0 & 0 & 0 & \cdots \\ \cdots & 0 & 0 & 0 & 0 & \alpha_{B,1}\beta_{B,1}\gamma_{B,1} & 0 & 0 & \cdots \\ & & & & \ddots & \ddots & \ddots & & \\ & & & \cdots & 0 & \alpha_{B,n-2}\beta_{B,n-2}\gamma_{B,n-2} & & & \\ & & & \cdots & 0 & \alpha_{B,n-1}\beta_{B,n-1}\gamma_{B,n-1} & & & \end{pmatrix}}_{\text{Matrix } \mathbf{A}} \underbrace{\begin{pmatrix} c_{A,n-1}^k \\ c_{A,n-2}^k \\ \vdots \\ c_{A,1}^k \\ c_{A,0}^k \\ c_{B,0}^k \\ c_{B,1}^k \\ \vdots \\ c_{B,n-2}^k \\ c_{B,n-1}^k \end{pmatrix}}_{\mathbf{x}} = \underbrace{\begin{pmatrix} c_{A,n-1}^{k-1} \\ c_{A,n-2}^{k-1} \\ \vdots \\ c_{A,1}^{k-1} \\ c_{A,0}^{k-1} \\ c_{B,0}^{k-1} \\ c_{B,1}^{k-1} \\ \vdots \\ c_{B,n-2}^{k-1} \\ c_{B,n-1}^{k-1} \end{pmatrix}}_{\mathbf{d}}$$

(Eq. 5.15)

Here, $\mathbf{A}$ is a dense matrix containing only constants, $\mathbf{x}$ is the unknown concentrations of timestep k and $\mathbf{d}$ is the known concentrations from the previous timestep. Notice that, to form a tridiagonal matrix, the alignment of the concentration values of the two species has to be ‘back-to-back’ with respect to the spatial domain, because they are interconnected only at the electrode interface.

The ultimate goal here is to find a set of solutions, represented by vector $\mathbf{x}$, at each of the iterative timesteps. The Thomas Algorithm is the solver to be introduced here; it is based on a more generalised Gaussian elimination method. The Thomas solver, different to the

Gaussian elimination method,⁶ make use of the diagonal pattern in the matrix and thus is specialised in solving diagonal matrixes efficiently.

For a discretised spatial grid containing n spatial coordinates, the size of the matrix $\mathbf{A}$, accounting for two species, is $2n$ by $2n$. By taking advantage of the tridiagonal pattern, the representation of matrix $\mathbf{A}$ can be simplified to three vectors ($\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$), each of size $2n$; the indexing of these vector elements follows the vertical index of the matrix.

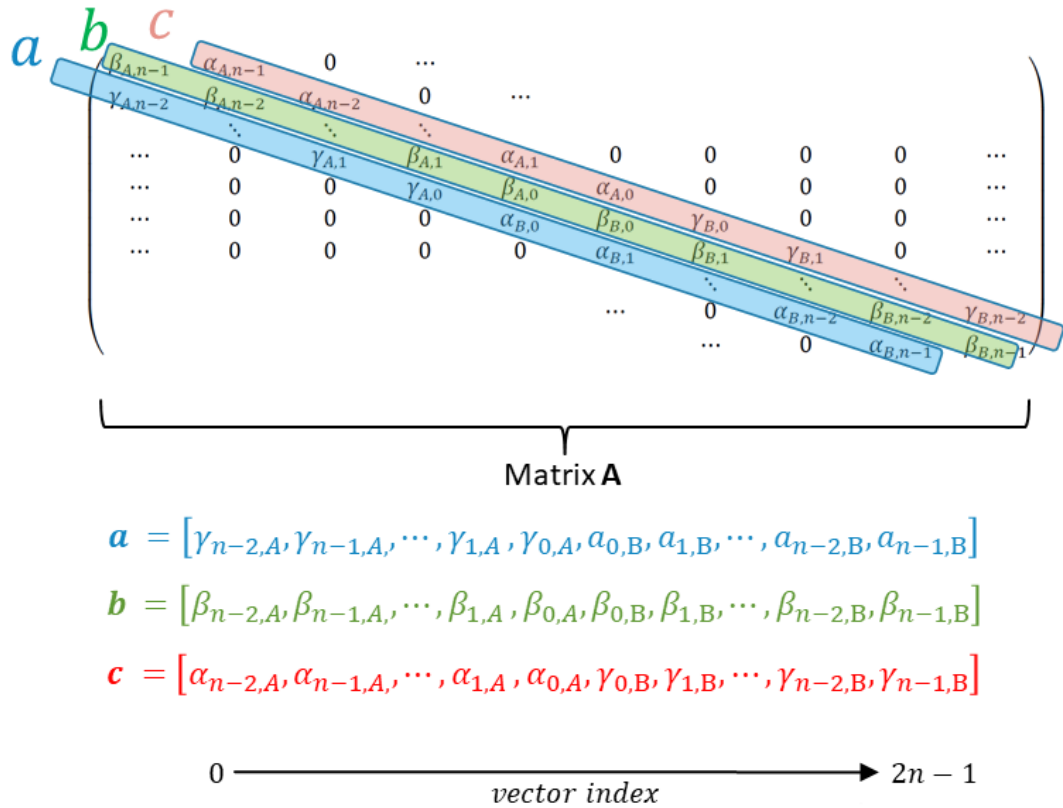


Figure 5.5. Schematic of a tridiagonal matrix $\mathbf{A}$ of size $2n$ by $2n$, and that represented by three vectors of size $2n$.

The use of three vectors $\mathbf{a}$, $\mathbf{b}$ and $\mathbf{c}$ to describe a large and sparse matrix ($\mathbf{A}$) will simplify the notation in the below-discussed matrix operations. Moreover, from a programmer's perspective, this significantly decreases the computational memory requirement approximately by a factor of n , where n is usually on the order of magnitude of hundreds for an expanding grid.

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First, the Thomas solver begins by factorising matrix $\mathbf{A}$, into two matrixes, a lower matrix $\mathbf{L}$ and an upper matrix $\mathbf{U}$.

$$\underbrace{\begin{pmatrix} b_0 & c_0 & & \\ a_1 & b_1 & c_1 & \\ & \ddots & \ddots & \ddots \\ & & a_{2n-2} & b_{2n-2} & c_{2n-2} \\ & & & a_{2n-1} & b_{2n-1} \end{pmatrix}}_{\mathbf{A}} = \underbrace{\begin{pmatrix} b'_0 & & & \\ a_1 & b'_1 & & \\ & \ddots & \ddots & \\ & & a_{2n-2} & b'_{2n-2} \\ & & & a_{2n-1} & b'_{2n-1} \end{pmatrix}}_{\mathbf{L}} \underbrace{\begin{pmatrix} 1 & c'_0 & \cdots & \\ & 1 & c'_1 & \\ & & \ddots & \ddots \\ & & & 1 & c'_{2n-2} \\ & & & & 1 \end{pmatrix}}_{\mathbf{U}} \quad (\text{Eq. 5.16})$$

The terms b'_i and c'_i in the $\mathbf{LU}$ matrix are modified and different to those in matrix $\mathbf{A}$. The matrix equation to be solved can be written as

$$\mathbf{LUx} = \mathbf{d} \quad (\text{Eq. 5.17})$$

Next, both sides of Equation 5.17 are multiplied by $\mathbf{L}^{-1}$

$$\mathbf{Ux} = \mathbf{d}' \quad (\text{Eq. 5.18})$$

where $\mathbf{d}' = \mathbf{L}^{-1}\mathbf{d}$. The matrix representation of Equation 5.18 is

$$\begin{pmatrix} 1 & c'_0 & & \\ & 1 & c'_1 & \\ & & \ddots & \ddots \\ & & & 1 & c'_{2n-2} \\ & & & & 1 \end{pmatrix} \begin{pmatrix} x_0 \\ x_1 \\ \vdots \\ x_{2n-2} \\ x_{2n-1} \end{pmatrix} = \begin{pmatrix} d'_0 \\ d'_1 \\ \vdots \\ d'_{2n-2} \\ d'_{2n-1} \end{pmatrix} \quad (\text{Eq. 5.19})$$

Computationally, the values of c'_i in matrix $\mathbf{U}$ can be first calculated

$$c'_i = \begin{cases} c_i/b_i & \text{for } i = 0 \\ c_i/(b_i - c'_{i-1}a_i) & \text{for } i = 1, 2, \dots, 2n-2 \end{cases} \quad (\text{Eq. 5.20})$$

The vector $\mathbf{d}'$ can be obtained by inversing matrix $\mathbf{L}$ before post-multiplying $\mathbf{d}$.

$$d'_i = \begin{cases} d_i/b_i & \text{for } i = 0 \\ (d_i - d'_{i-1}a_i)/(b_i - c'_{i-1}a_i) & \text{for } i = 1, 2, \dots, 2n-1 \end{cases} \quad (\text{Eq. 5.21})$$

At this point, all the elements in matrix equation 5.18 (and 5.19) have been computed.

The next step is to multiply each side of Equation 5.18 by $\mathbf{U}^{-1}$ to give

$$\mathbf{x} = \mathbf{U}^{-1}\mathbf{d}' \quad (\text{Eq. 5.22})$$

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Finally, the set of solutions for vector $\mathbf{x}$, representing all the unknown concentration values of $c_{A,i}^k$ and $c_{B,i}^k$ over the whole spatial domain, can be computed at once:

$$x_i = \begin{cases} d'_{2n-1} & \text{for } i = 2n - 1 \\ d'_i - c'_i x_{i+1} & \text{for } i = 2n - 2, 2n - 3, \dots, 0 \end{cases} \quad (\text{Eq. 5.23})$$

The following processes are repeated at each iterative timestep until the end of the simulation. The method described herein can be generalised to multidimensional diagonal matrixes.²

Hitherto, the mathematics discussed in this Chapter formulates the basis to solve *any* kinetic-diffusion electrochemical systems, as long as the matrix equations are *linear*. The term ‘linear’ here refers to the linearity of the set of simultaneous equations to be solved; examples of non-linear equations, and the solution to which, are shown in the next section.

5.4 Multidimensional Root Finding: Newton-Raphson Method

The mathematical problem for a simple electrochemical system, $A(aq) + e^- \rightleftharpoons B(aq)$, involving only the heterogeneous electron transfer and mass transport is considered to be linear, and can be solved directly by using the Thomas Algorithm as seen above. An example of a *non-linear* mathematical problem includes bi-molecular homogeneous reactions or surface adsorption (more in Chapter 6 and 7).

Below are examples of non-linear simultaneous equations needing to be solved when 2nd order reaction kinetics are involved, $A(aq) + Y(aq) \xrightarrow{k_{2nd}} \text{Product}$.

$$\begin{aligned}
 & \vdots \\
 c_{A,i+1}^{k-1} &= \alpha_{i+1} c_{A,i}^k + \beta_{i+1} c_{A,i+1}^k + \gamma_{i+1} c_{A,i+2}^k - k_{2nd} \Delta t c_{A,i+1}^k c_{Y,i+1}^k \\
 c_{A,i}^{k-1} &= \alpha_i c_{A,i-1}^k + \beta_i c_{A,i}^k + \gamma_i c_{A,i+1}^k - k_{2nd} \Delta t c_{A,i}^k c_{Y,i}^k \\
 c_{A,i-1}^{k-1} &= \alpha_{i-1} c_{A,i-2}^k + \beta_{i-1} c_{A,i-1}^k + \gamma_{i-1} c_{A,i}^k - k_{2nd} \Delta t c_{A,i-1}^k c_{Y,i-1}^k \\
 & \vdots
 \end{aligned}$$

$\underbrace{\hspace{15em}}$
 Linear terms
(diffusion)

$\underbrace{\hspace{15em}}$
 Non-linear term
(second-order reaction)

(Eq. 5.24)

The non-linearity results from the terms involving two unknown and independent variables. To solve the set of non-linear simultaneous equations, one has to first linearise the matrix equation before it gets ‘fed’ it into the Thomas solver. Here is where the Newton-Raphson method, one of the simplest but accurate multidimensional root-finding methods, comes to the rescue.

The mathematic concept of this root finding method is not too difficult to understand. Let us first consider a mathematical function $f(x)$ which has a real root at $x = r$, i.e. $f(r) = 0$. Providing an initial estimate of the root value, x_0 , is sufficiently close to the root value

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r . Then Newton-Raphson acts iteratively to improve and correct the previous estimation by δx until the function approaches to the real root value r with sufficient accuracy.

The Taylor expansion of $f(x_0 + \delta x)$ is

$$f(x_0 + \delta x) = f(x_0) + f'(x_0)\delta x + \frac{f''(x_0)}{2!}\delta x^2 + \dots \quad (\text{Eq. 5.25})$$

If δx is sufficiently small, the higher-order terms involving δx are negligible, giving

$$f(x_0 + \delta x) \approx f(x_0) + f'(x_0)\delta x \quad (\text{Eq. 5.26})$$

Then, providing that the initial guess not too far from the root value, then $f(x_0 + \delta x)$ is $= 0$

$$f(x_0 + \delta x) = f(x_0) + f'(x_0)\delta x = 0 \quad (\text{Eq. 5.27})$$

Rearranging for δx and adding x_0 to both side

$$x_1 = x_0 + \delta x = x_0 - \frac{f(x_0)}{f'(x_0)} \quad (\text{Eq. 5.28})$$

where x_1 is an improved estimate from x_0 after one iteration. This process is repeated until the changes from the last guess is minimal and has reached a satisfactory level, usually defined as the tolerance level ε . An illustrative diagram of the iterative root finding method is shown in Figure 5.6.

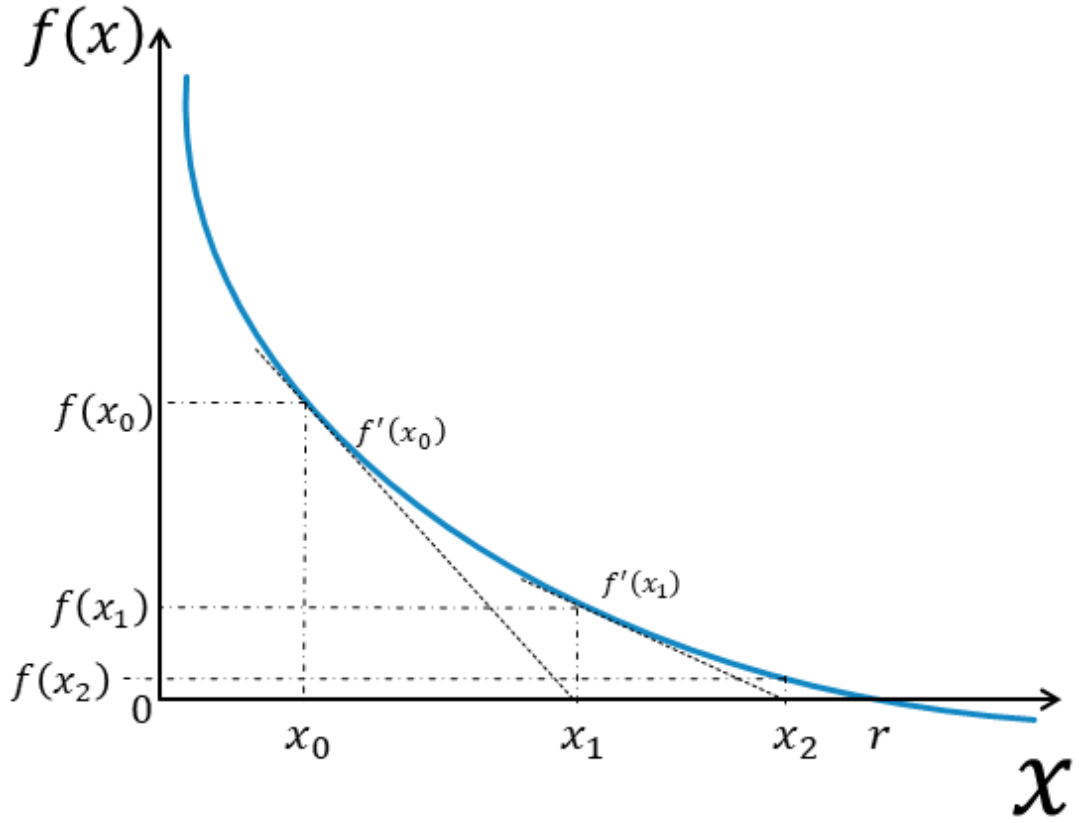


Figure 5.6. Illustration of an iterative root finding method. Here, two iterations from the initial guess x_0 are shown.

The Newton-Raphson method is not limited to a one-dimensional function $f(x)$, but can be extended to N simultaneous equations with N variables. Let us return to the example set of non-linear Equations (5.24), by rearranging all terms to the right-hand side the equations are now equated to zero.

$$\begin{aligned}
 & \vdots \\
 f_{i+1} &= \alpha_{i+1} c_{A,i}^k + \beta_{i+1} c_{A,i+1}^k + \gamma_{i+1} c_{A,i+2}^k - k_{2nd} \Delta t c_{A,i+1}^k c_{Y,i+1}^k - c_{A,i+1}^{k-1} \\
 f_i &= \alpha_i c_{A,i-1}^k + \beta_i c_{A,i}^k + \gamma_i c_{A,i+1}^k - k_{2nd} \Delta t c_{A,i}^k c_{Y,i}^k - c_{A,i}^{k-1} \\
 f_{i-1} &= \alpha_{i-1} c_{A,i-2}^k + \beta_{i-1} c_{A,i-1}^k + \gamma_{i-1} c_{A,i}^k - k_{2nd} \Delta t c_{A,i-1}^k c_{Y,i-1}^k - c_{A,i-1}^{k-1} \\
 & \vdots
 \end{aligned} \tag{Eq. 5.29}$$

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Equations above (5.29) can be view as a set of N non-linear simultaneous equations waiting to be zeroed:

$$f_i(x_0, x_1, x_2, x_3, \dots, x_{N-1}) = 0, \text{ for } 0 \leq i < N \quad (\text{Eq. 5.30})$$

Here $x_0, x_1, x_2 \dots x_{N-1}$ represents the N unknown concentrations. Analogues to Equation 5.26, the set of non-linear simultaneous equations can be written as

$$f_i(\mathbf{x} + \delta\mathbf{x}) \approx f_i(\mathbf{x}) + \sum_{j=0}^{N-1} \left(\frac{\partial f_i}{\partial x_j} \delta x_j \right), \text{ for } 0 \leq i < N \quad (\text{Eq. 5.31})$$

where $\mathbf{x}$ is the vector of the N unknown concentrations, and $\delta\mathbf{x}$ is a vector containing the correction to the previous estimates. Alternatively, to aid visualisation, it can be written in the matrix form

$$\mathbf{F}(\mathbf{x} + \delta\mathbf{x}) = \mathbf{F}(\mathbf{x}) + \mathbf{J}\delta\mathbf{x} \quad (\text{Eq. 5.32})$$

The vector function $\mathbf{F}$ represents the series of functions to be zeroed and $\mathbf{J}$, known as the Jacobian, is a N by N matrix containing partial derivatives

$$\mathbf{J} = \begin{pmatrix} \frac{\partial f_0}{\partial x_0} & \frac{\partial f_0}{\partial x_1} & \frac{\partial f_0}{\partial x_2} & \dots & \frac{\partial f_0}{\partial x_{N-1}} \\ \frac{\partial f_1}{\partial x_0} & \frac{\partial f_1}{\partial x_1} & \frac{\partial f_1}{\partial x_2} & \dots & \frac{\partial f_1}{\partial x_{N-1}} \\ \frac{\partial f_2}{\partial x_0} & \frac{\partial f_2}{\partial x_1} & \frac{\partial f_2}{\partial x_2} & \dots & \frac{\partial f_2}{\partial x_{N-1}} \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ \frac{\partial f_{N-1}}{\partial x_0} & \frac{\partial f_{N-1}}{\partial x_1} & \frac{\partial f_{N-1}}{\partial x_2} & \dots & \frac{\partial f_{N-1}}{\partial x_{N-1}} \end{pmatrix} \quad (\text{Eq. 5.33})$$

Therefore, the matrix equation to be solved is

$$\mathbf{J}\delta\mathbf{x} = -\mathbf{F}(\mathbf{x}) \quad (\text{Eq. 5.34})$$

The Jacobian matrix initial looks intimidating, but it is pretty straightforward to formulate by hand. Once the Jacobian has been worked out, it usually results in either a tridiagonal

or multidimension diagonal matrix, containing only linear terms. The non-linear set of simultaneous equations is now linearised. Analogue to the matrix shown in Equation 5.15, the Jacobian can be ‘fed’ into the Thomas solver to obtain the vector of improvement $\delta\mathbf{x}$ to the previous estimates, the process then repeats with an improved vector of estimation ($\mathbf{x} + \delta\mathbf{x}$) until the tolerance level are satisfied.

5.5 Error and Convergence

After implementing the codes to run an electrochemical simulation programme, using the coding language of preference, the user is responsible for testing the simulation programme thoroughly.⁷ Any logical error in the simulation program, large or small, is better to be rectified as early as possible. The possible errors can be mathematical, bad coding or even a single typo within thousands of lines of code. Although this can be a tedious process, it is the most important part of programming. For the simulation models and results presented in Chapters 6 and 7, the following tests for possible error and convergence are conducted to ensure the program is ‘good to go’.

The error and convergence tests include:

- Mass conservation over the entire temporal domain. This can be easily implemented in the code the user gets notified if and when this is breached.
- Compare simulated results to that obtained from analytical expressions; this is discussed in more detail when the specific electrochemical models are discussed in Chapter 6 and 7.
- Variation of spatial and temporal resolution (Δx and Δt) to see if the results are converged to a constant value. This is typically repeated over the range of simulation parameters intended for result and discussion.
- If Newton-Raphson method is used, the variation of tolerance level (ε) is to be part of the convergence test.

Now the mathematical tools enabling one to numerically simulate non-linear electrochemical problems have been introduced, the next Chapter commences to provide new insights from simulation, how adsorption can affect voltammetry.

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Chapter 6 Voltammetry of Adsorbed Species: Ideal Interactions

Within the wealth of possible electrochemical processes, adsorption on surface sites of electrodes are, arguably, one of the most difficult phenomena to be analysed from experimental data alone because the voltammetric signal can be entangled with, possibly, a combination of electron transfer, adsorption kinetics and mass transport limitations. In this Chapter, a general simulation model is developed for voltammetry of species adsorbed from solution involving coupled mass transport and adsorption which distinguishes the relative contributions from the adsorption kinetics, the mass transport and the electron transfer kinetics of the reactants and products.

The Chapter begins with an introduction to adsorption in voltammetry and an overview of the simulation work in this field. Then, the theory section outlines the simulation model which is solved with the numerical methods as discussed in Chapter 5. To provide meaningful insights from simulation, this study focuses on three limiting cases in which the fate of the formed product differs. In Case One, the product remains on the surface and does not desorb; in Case Two, the product desorbs slowly into solution; in Case Three, the product desorbs rapidly into solution.

The results presented in this Chapter were published in the *Journal of Electroanalytical Chemistry*, which has granted full reuse permission for the purpose of this thesis.¹

6.1 Introduction

In voltammetry involving adsorbed species, the possible simultaneously occurring electron transfer via an outer-sphere mechanism, finite adsorption/desorption kinetics and mass transport can severally ‘muddy the water’ when it comes to analysing the surface peaks.^{2, 3} Such a phenomenon was first considered by Brdička *et al.*, where reversible pre-waves (or post-waves) were seen on mercury electrodes.⁴⁻⁶ He considered the case where the solution contains only one redox-active reactant, complicated by an alternative electron-transfer pathway via the adsorbed state (located at the Inner-Helmholtz Plane), in addition to the outer-sphere mechanism, which can result in either a pre-wave or post-wave depending which adsorbs more strongly, the product or the reactant.³

Adsorption is not uncommon in analytical electrochemistry and has significant interest across scientific and commercial applications.⁷⁻¹¹ For example, the naturally occurring redox-active organic compounds responsible for the characteristic taste of turmeric,¹² garlic¹³ and chilli¹⁴ have been electrochemically targeted and analysed, some with commercial success.¹⁵ The corresponding redox-active organic compounds targeted were gingerol, thiosulfinates and capsaicin, as a measure of ‘strength’ or ‘hotness’ of its corresponding organic matter; in all cases, they were all found to adsorb onto the surface of the electrode. Moreover, the metal-deposition forming a monolayer of adatom on the foreign surface (support), more of which discussed later in Chapter 7, has tremendous value in the field of catalysis and surface chemistry.¹¹ Thus, understanding the roles of adsorption in voltammetry, especially the resulting current response and peak-shape is vital in electrochemistry.

The pioneering and seminal works by Laviron and co-workers have contributed extensively to the understanding of electrochemical processes that occur on an electrode surface, especially when both the reactants and products are strongly adsorbed – which

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is often the case on mercury electrodes.^{16, 17} Their work includes, but is not limited to, simulation of various type of EC reactions (electrochemical reactions followed by chemical reactions) on the electrode surface.¹⁸⁻²³ Developing mathematical theory to understand of the role of adsorption on rotating disk voltammetry, assuming a fast and non-rate-determining adsorption step.^{24, 25} Alternating current polarography and a Faradaic impedance study of strongly adsorbed electroactive species.²⁶⁻²⁹

More recent development in this field includes the modelling of the one-step electrodeposition reaction by Pekka *et al.* Their work investigates the linear sweep voltammetry of the soluble-insoluble system with the generation of working curves which were used to extract kinetic information of the $\text{Cu}_{(\text{aq})}^+/\text{Cu}_{(\text{s})}$ redox couple in acetonitrile.³⁰ Furthermore, the simulation by Chevallier *et al.* considers the adsorption kinetics of the reactant coupled with mass transport, where the product remains adsorbed on the surface.² This model examined all six of the independent control parameters and investigated how these affect the voltammetric shape; the six independent parameters studied were voltage scan rate, adsorption rate constant, equilibrium constant, standard electron transfer rate constant, saturation parameter and the initial coverage of species. The theory explained the adsorption behaviour observed during the reduction of aqueous $[\text{Co}(\text{NH}_3)_6]^{3+}$ at fast voltage scan rates.³¹

This work presents a general model for voltammetry which includes adsorbed species. The work advances from Chevallier *et al.* by considering the finite kinetics of adsorption and desorption of *both* the reactant and product, the electron transfer kinetics and the mass transport to and from the bulk solution. Herein, despite only the adsorbed species are assumed electrochemically active (i.e. no electron-transfer via the outer-sphere mechanism) the model still contains a total of nine independent parameters from which is obviously impossible to produce full working surfaces considering all of the

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parameters! To provide a meaningful insight of how the adsorption kinetics affect the current-voltage curve, the simulation focuses on *three* limiting cases in which the ‘fate’ of the product differs. In Case One, the product remains on the surface and does not desorb; in Case Two, the product slowly desorbs into the solution and in Case Three, the product desorbs rapidly into solution. For each case, the effect of independent parameters such as the adsorption rate constant of the reactant, the electron transfer kinetics and the voltage scan rate are investigated.

6.2 Theory

This section introduces the theoretical model employed for the simulations. The simulation considers only the surface-bound species to be electrochemically active. That is, the solution species must adsorb onto an available surface site prior to electron transfer.

6.2.1 Theoretical Model

An overview of the simulation model is depicted in Figure 6.1. The model contains two species, A and B , in the solution phase with bulk concentrations $c_{A,bulk}$ and $c_{B,bulk}$. The surface concentrations of the species at the electrode-solution interface are $c_{A,0}$ and $c_{B,0}$, from where they can adsorb onto the electrode with an adsorption rate constant of $k_{ads}^{A/B}$ ($\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$). The surface-bound species can either undergo redox reaction with a standard electrochemical rate constant k_0 or desorb into solution with a desorption rate constant of $k_{des}^{A/B}$ (s^{-1}).

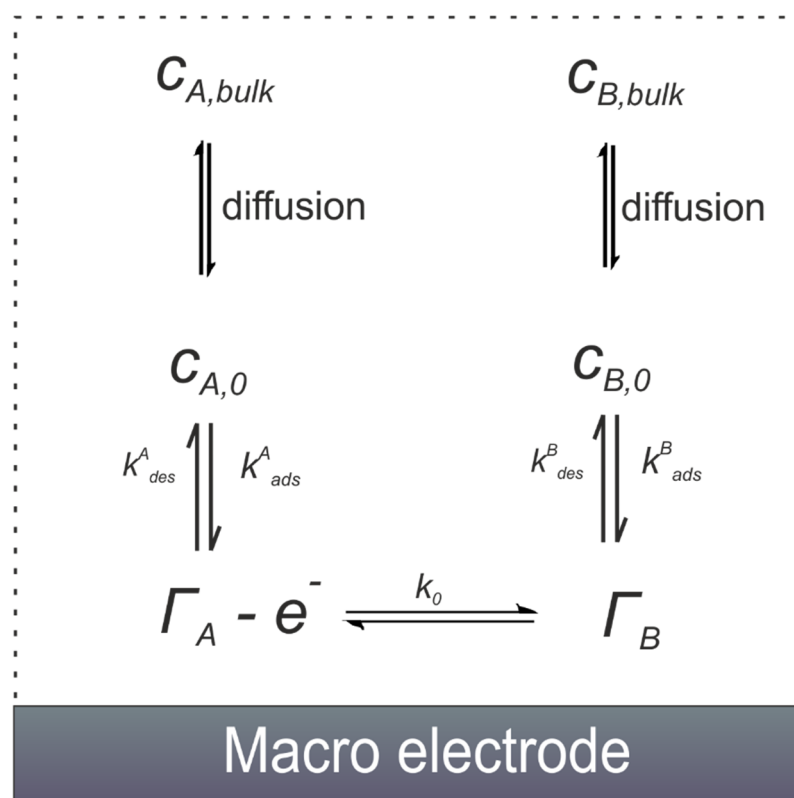


Figure 6.1. A schematic of the simulation model. The surface-bound of $A(ads)$ and $B(ads)$ are represented by Γ_A and Γ_B (mol m^{-2}), respectively.

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In this Chapter, the simulation model first adopts the Langmuir adsorption isotherm,³² which is a limiting case of the Frumkin adsorption isotherm when the net surface interactions between adsorbates is equal to zero.^{33, 34} This allows the mechanistic pathways and its effects on voltammetry be studied without excessively complexing the model. The effect of non-ideal surface interactions is discussed more later in Chapter 7. Moreover, the number of adsorption sites and the binding in this model are assumed independent of the applied potential. The unoccupied sites are presumed competitively accessible to both adsorbates until a maximum surface coverage Γ_{max} (mol m⁻²) is reached, where one adsorbate occupies one site. The simulation assumes only the adsorbed A and B are electrochemically active as indicated in Figure 6.1. Thus the time-dependent equations that describe the rate of interfacial reactions, adsorption and desorption are

$$\begin{aligned}\frac{\partial \Gamma_A}{\partial t} &= -k_{ox} \Gamma_A + k_{red} \Gamma_B + k_{ads}^A c_{A,0} (\Gamma_{max} - \Gamma_A - \Gamma_B) - k_{des}^A \Gamma_A \\ \frac{\partial \Gamma_B}{\partial t} &= k_{ox} \Gamma_A - k_{red} \Gamma_B + k_{ads}^B c_{B,0} (\Gamma_{max} - \Gamma_A - \Gamma_B) - k_{des}^B \Gamma_B \\ D_A \left(\frac{\partial c_{A,0}}{\partial x} \right)_{x=0} &= k_{ads}^A c_{A,0} (\Gamma_{max} - \Gamma_A - \Gamma_B) - k_{des}^A \Gamma_A \\ D_B \left(\frac{\partial c_{B,0}}{\partial x} \right)_{x=0} &= k_{ads}^B c_{B,0} (\Gamma_{max} - \Gamma_A - \Gamma_B) - k_{des}^B \Gamma_B \quad (Eq. 6.1)\end{aligned}$$

where t is the time from the start of the voltammetric sweep, x is the distance from the electrode surface and $\Gamma_{A/B}$ is the surface coverage of A or B . In the absence of convection and with sufficient supporting electrolyte, the mass transport of A and B to and from the semi-infinite bulk is described by Fick's second law

$$\begin{aligned}\left(\frac{\partial c_{A,0}}{\partial t} \right) &= D_A \frac{\partial^2 c_{A,0}}{\partial x^2} \\ \left(\frac{\partial c_{B,0}}{\partial t} \right) &= D_B \frac{\partial^2 c_{B,0}}{\partial x^2} \quad (Eq. 6.2)\end{aligned}$$

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The electrode kinetics of surface redox processes can be successfully described by the asymmetric Marcus-Hush model to give physical insights such as the ‘re-organisation energy’ which account for the curvature of Tafel slope at high over-potentials.³⁵⁻³⁸ For small applied over-potentials, however, the Tafel slope is typically linear and thus can be described by the semi-empirical Butler-Volmer kinetics³⁹⁻⁴¹

$$\begin{aligned} k_{ox} &= k_0 e^{\frac{\beta F}{RT}(E-E_f^0)} \\ k_{red} &= k_0 e^{\frac{-(1-\beta)F}{RT}(E-E_f^0)} \end{aligned} \quad (Eq. 6.3)$$

where the electron transfer rate constants k_{ox} and k_{red} varies exponentially with a transfer coefficient β and the applied potential E . The Butler-Volmer kinetics is used here for ease of computation and to explore the role of finite adsorption kinetics. The formal potential E_f^0 is defined as the potential at which the surface coverages $\Gamma_A = \Gamma_B$ at equilibrium.⁴² This is because the net rate of electron-transfer is zero at equilibrium

$$0 = -k_{ox} \Gamma_A + k_{red} \Gamma_B \quad (Eq. 6.4)$$

Substituting Equation 6.3 into Equation 6.4 followed by rearrangement gives

$$k_0 e^{\frac{\beta F}{RT}(E-E_f^0)} \Gamma_A = k_0 e^{\frac{-(1-\beta)F}{RT}(E-E_f^0)} \Gamma_B \quad (Eq. 6.5)$$

Taking the natural logarithm on both sides, an expression for $E - E_f^0$ can be obtained with further rearrangement

$$E - E_f^0 = \frac{RT}{F} \ln \left(\frac{\Gamma_B}{\Gamma_A} \right) \quad (Eq. 6.6)$$

It is clear from Equation 6.6 that, when the applied potential E equals E_f^0 , the surface coverage of A is equal to B .

At the start of the simulation, species A is present uniformly throughout the solution

$$t = 0, \quad 0 \leq x \leq \infty \quad \begin{cases} c_{A,x} = c_{A,bulk} \\ c_{B,x} = 0 \end{cases} \quad (Eq. 6.7)$$

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The simulation assumes sufficient time was allowed before any measurement for the surface coverage Γ_A to reach equilibrium with $c_{A,bulk}$

$$t = 0 \quad \begin{cases} \Gamma_{A,pre-adsorbed} = \frac{k_{ads}^A c_{A,bulk} \Gamma_{max}}{k_{ads}^A c_{A,bulk} + k_{des}^A} \\ \Gamma_{B,pre-adsorbed} = 0 \end{cases} \quad (Eq. 6.8)$$

During a cyclic voltammetry simulation, the potential applied to the electrode E varies linearly with time

$$E = E_{initial} + vt \quad (Eq. 6.9)$$

here $E_{initial}$ is the starting potential and v is the scan rate. At time $t = t_{switch}$, the potential reaches E_{switch} and the potential sweep changes direction

$$E = E_{switch} - v(t - t_{switch}) \quad (Eq. 6.10)$$

During the cyclic voltammetry, the current I reflects the contribution from the net flux of the redox processes occurring on the electrode surface

$$\frac{I}{FA} = j = k_{ox} \Gamma_A - k_{red} \Gamma_B \quad (Eq. 6.11)$$

where F is the Faraday constant and A is the area of the electrode. To generalise the simulation results for the broad range of experimental parameters, dimensionless parameters will be used. The required normalization of the dimensioned parameters is discussed in the next section.

6.2.2 Normalised Parameters

Dimensionless parameters will be used to characterize the simulated voltammograms.

The advantages in using dimensionless parameters as opposed to dimensional parameters is that; first, the number of independent parameters is reduced to a minimum and consequently, second, the number of simulations required to describe a wide range of experimental conditions is reduced.

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Table 6.1 shows the dimensional parameters which are used for the normalizations shown in Table 6.2.

Table 6.1. Dimensional parameters

Dimensional parameters	
t	time (s)
x	distance from the electrode surface (m)
r_e	radius of the electrode (m)
c_j	concentration of species j (mol m ⁻³)
Γ_j	surface coverage of species j (mol m ⁻²)
k_0	standard electron transfer rate constant (s ⁻¹)
k_{ads}^j	adsorption rate constant of species j (m ³ mol ⁻¹ s ⁻¹)
k_{des}^j	desorption rate constant of species j (s ⁻¹)
D_j	diffusion coefficient of species j (m ² s ⁻¹)
v	scan rate (V s ⁻¹)
E_f^0	formal potential (V)
j	flux of electrons (mol m ⁻² s ⁻¹)
I	current (A)

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Table 6.2. Dimensionless parameters and definitions

Dimensionless parameters		Normalisation
T	time	$D_A t / r_e^2$
X	spatial coordinates	x / r_e
C_j	concentration of species j	$c_j / c_{j,bulk}$
θ_j	fractional surface coverage of species j	Γ_j / Γ_{max}
K_0	standard electron transfer rate constant	$\frac{k_0 r_e^2}{D_A}$
K_{ads}^j	adsorption rate constant of species j	$\frac{k_{ads}^j \Gamma_{max} r_e}{D_A}$
K_{des}^j	desorption rate constant of species j	$\frac{k_{des}^j \Gamma_{max} r_e}{D_A c_{A,bulk}}$
d_j	diffusion coefficient	D_j / D_A
σ	scan rate	$(r_e^2 / D_A)(F / RT)v$
B	saturation parameter	$c_{A,bulk} r_e / \Gamma_{max}$
Θ	potential applied	$(F / RT)(E - E_f^0)$
J	flux	$\frac{I}{\pi r_e F D_A c_{A,bulk}}$

The equations formulating the mathematical model can be expressed in the dimensionless forms

$$\frac{\partial \theta_A}{\partial T} = -K_{ox} \theta_A + K_{red} \theta_B + K_{ads}^A B C_{A,0} (1 - \theta_A - \theta_B) - K_{des}^A B \theta_A$$

$$\frac{\partial \theta_B}{\partial T} = K_{ox} \theta_A - K_{red} \theta_B + K_{ads}^B B C_{B,0} (1 - \theta_A - \theta_B) - K_{des}^B B \theta_B$$

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$$\begin{aligned}
 \left(\frac{\partial C_A}{\partial X}\right)_{X=0} &= K_{ads}^A C_{A,0} (1 - \theta_A - \theta_B) - K_{des}^A \theta_A \\
 \left(\frac{\partial C_B}{\partial X}\right)_{X=0} &= \frac{K_{ads}^B}{d_B} C_{B,0} (1 - \theta_A - \theta_B) - \frac{K_{des}^B}{d_B} \theta_B \\
 \left(\frac{\partial C_A}{\partial T}\right)_{X>0} &= \frac{\partial^2 C_A}{\partial X^2} \\
 \left(\frac{\partial C_B}{\partial T}\right)_{X>0} &= d_B \frac{\partial^2 C_B}{\partial X^2}
 \end{aligned} \tag{Eq. 6.12}$$

The initial conditions in the dimensionless form are shown in Table 6.3.

Table 6.3. Initial simulation conditions.

Equations	Boundary regions
$C_A = 1$	$0 \leq X \leq \infty, \quad T = 0$
$C_B = 0$	$0 \leq X \leq \infty, \quad T = 0$
$\theta_A = \theta_{A, \text{ pre-adsorbed}}$	$T = 0$
$\theta_B = 0$	$T = 0$

where $\theta_{A, \text{ pre-adsorbed}}$ is the dimensionless coverage of A at adsorption equilibrium prior to the start of the simulation

$$\theta_{A, \text{ pre-adsorbed}} = \frac{K_{ads}^A C_{A,bulk}}{K_{ads}^A C_{A,bulk} + K_{des}^A} \tag{Eq. 6.13}$$

Notice below the subtle but important difference between the uppercase Θ representing for dimensionless potential and the lowercase θ for fractional coverage. The dimensionless potential Θ varies linearly with dimensionless time T and dimensionless scan rate σ similar to Equation 6.9 and 6.10

$$\begin{aligned}
 \Theta &= \Theta_{initial} + \sigma T \\
 \Theta &= \Theta_{switch} - \sigma(T - T_{switch})
 \end{aligned} \tag{Eq. 6.14}$$

The dimensionless flux J at the electrode surface is

$$J = \frac{1}{B}(K_{ox}\theta_A - K_{red}\theta_B) \quad (Eq.6.15)$$

where B is a “saturation” parameter that links surface coverage and concentration (see Table 6.2). The dimensionless flux J can then be converted back to the dimensional current I via

$$I = \pi r_e F D_A c_{A,bulk} J \quad (Eq. 6.16)$$

Next section discusses the approach to solving the set of partial equations subject to the boundary conditions of interest and the convergence studies.

6.2.3 Numerical Simulation and Convergence

The partial differential equations for this one-dimensional system were discretized using the backwards-implicit method, as discussed in Section 5.2, with a uniform temporal grid and a spatial grid that expands exponentially from the electrode surface to

$$X_{max} = 6\sqrt{T_{max}} \quad (Eq.6.17)$$

where T_{max} is the dimensionless duration of the cyclic voltammetry scan and X_{max} is a dimensionless distance defined well-beyond the thickness of the diffusion layer during the timescale of voltammetry.⁴³ The sets of discretized diffusion equations were solved using the extended Thomas algorithm, introduced in Section 5.3.^{44, 45}

The simulation model was validated with tests that benchmark each constituent part of the model.⁴⁶ For a fully reversible surface-bound redox system, the analytical expression of the dimensional peak current is $\frac{n^2 F^2 v}{4RT} A \Gamma_{max}$,⁴⁷ where n is the number of electron transferred and A is the area of the electrode; this can be converted to the dimensionless form to give the expression for peak flux of $\sigma/4B$. The surface-bound redox processes in the simulation model were first tested by setting a fast electron transfer rate constant K_0 relative to mass transport and all the adsorption and desorption rate constants

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$(K_{ads}^A, K_{des}^A, K_{ads}^B, K_{des}^B)$ to zero, and the initial surface coverage of θ_A to unity. The simulated peak flux is within 1% of $\sigma/4B$, in agreement with the analytical expression. Second, the diffusion of the species from the bulk were tested by applying an overpotential at $T = 0$ with the rate of adsorption and desorption set to a high value such that the mass transport rate to the electrode becomes the rate-limiting step; this results in a current transient described by the Cottrell equation.⁴⁸ Finally, the conservation of mass was checked and was conserved throughout all of the simulations. The values of the incremental spatial and temporal point were set to a small value to ensure numerical convergence. The simulations were ran on a dual Intel (R) Core (TM) E5-2640 v4 CPU with 16.00 GB of RAM, the time for a typical simulation is approximately three minutes.

6.2.4 Analytical Solution for Case One Under Irreversible Electron Transfer Kinetics

In this sub-section, the analytical expression for Case One under irreversible electrode kinetics is derived. At a very high adsorption rate constant K_{ads}^A and under irreversible electron transfer kinetics, the dimensionless oxidative peak flux J for Case One plateaued to a value of 1.84×10^{-3} , as can be seen in Figure 6.4 b).

As the rate of adsorption K_{ads}^A approaches ∞ , the equilibrium coverage $\theta_{A, equilibrium}$ prior to the simulation approaches unity (Equation 6.13). Therefore, the boundary conditions at the start of the simulation are

$$T = 0, \begin{cases} \theta_A = 1 \\ \theta_B = 0 \end{cases} \quad (Eq. 6.18)$$

Under irreversible electron transfer kinetics, the dimensionless flux J reduces from Equation 6.15 to

$$J = -\frac{1}{B} \frac{d\theta_A}{dT} \approx \frac{1}{B} K_{ox} \theta_A, \quad \text{where } K_{ox} = K_0 e^{\beta\theta(T)} \text{ and } \theta(T) = \theta_{initial} + \sigma T \quad (Eq. 6.19)$$

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which can be rearranged to

$$\frac{1}{\theta_A} d\theta_A = -K_0 e^{\beta(\theta_{initial} + \sigma T)} dT \quad (Eq. 6.20)$$

Integrating both sides with the initial boundary conditions given in Equation 6.18 leads to an expression for the surface coverage θ_A as a function of time T

$$\theta_A(T) = \exp\left(c(e^{\beta\sigma T} - 1)\right) \text{ where } c = -\frac{K_0 e^{\beta\theta_{initial}}}{\beta\sigma} \quad (Eq. 6.21)$$

where c is a constant and independent to time T . The differential of Equation 6.21 with respect to time T gives an expression for the dimensionless flux J as a function of time T

$$J(T) = \frac{\beta\sigma c}{B} e^{\beta\sigma T} e^{c(e^{\beta\sigma T} - 1)} \quad (Eq. 6.22)$$

When the flux J reaches a maximum during the oxidation sweep, the derivative of $J(T)$ with respect to time T is equal to zero

$$\frac{dJ(T)}{dT} = \frac{(\beta\sigma)^2 c e^{\beta\sigma T} e^{c(e^{\beta\sigma T} - 1)}}{B} (1 + c e^{\beta\sigma T}) = 0 \quad (Eq. 6.23)$$

Substituting the constant c from Equation 6.21 into Equation 6.23 with further simplification gives

$$1 = \frac{K_0 e^{\beta\theta_{peak}}}{\beta\sigma} \quad (Eq. 6.24)$$

which can be rearranged to give an expression for the dimensionless θ_{peak}

$$\theta_{peak} = \frac{1}{\beta} \ln\left(\frac{\beta\sigma}{K_0}\right) \quad (Eq. 6.25)$$

Finally, substituting the dimensionless peak potential θ_{peak} and the constant c back into the expression for flux J (Equation 6.22) gives an expression for the peak flux J_{peak}

$$J_{peak} = \frac{\beta\sigma}{B} e^{-1} \quad (Eq. 6.26)$$

6.3 Results and Discussions

The full model illustrated in Figure 6.1 contains nine independent variables, namely K_0 , K_{des}^A , K_{ads}^A , K_{des}^B , K_{ads}^B , d_B , β , σ and B . A fully general working surface for the current-voltage curve, reflecting all combinations of those independent variables is clearly neither possible to realistically generate nor useful in the understanding of the curves. Rather for the latter purposes, the model focuses on three limiting cases which reduce the complexity as well as provide meaningful physico-chemical insights. In all cases, only species A is present in the bulk solution and equilibrium is reached with the surface coverage of A before the voltammetry “experiment” being commenced. Cyclic voltammograms are then simulated with the applied potential varying linearly with time in a triangular wave shape. The differences between the three limiting cases considered are the extent to which the surface-bound product θ_B diffuses into the bulk solution; in case one, the θ_B remains on the surface and does not desorb; in case two, θ_B slowly desorbs into solution; in case three, θ_B desorbs rapidly into the solution.

6.3.1 Case One – Species B Remains on the Surface

In the first limiting case, the surface-bound species B remains on the surface. A schematic of the simplified processes is shown in Figure 6.2. The number of independent parameters reduced down to K_0 , K_{des}^A , K_{ads}^A , β , σ and B . The work by Chevallier *et al.* provided a general quantitative view of Case One for a micro-electrode by, effectively, examining all the independent parameters using two to three values for each of the parameters.² In the present study, the adsorption rate constant K_{ads}^A , the electron transfer rate constant K_0 and the scan rate σ are studied in-depth to see how they affect the shape and peak size

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of the voltammograms. The other parameters are set constant: $K_{des}^A = 1$, $d_B = 1$, $\beta = 0.5$ and $B = 100$.

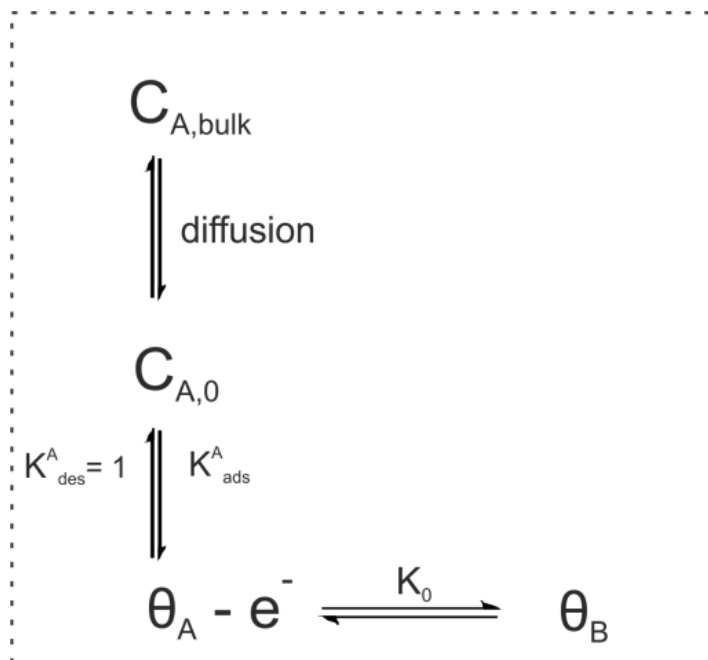


Figure 6.2. The reaction mechanism for Case One, where product B is exclusively surface-bound.

Figure 6.3 a) shows the simulated cyclic voltammograms under *fast* and ‘reversible’ electron transfer kinetics with different adsorption rate constants K_{ads}^A . Note, the term *fast* or *slow* electron transfer kinetics here is *relative* to the rate of mass transport from the bulk solution.⁴⁹

The simulation assumes adsorption equilibrium was reached prior to the start of the simulation. For a small adsorption rate constant of A, relative to the corresponding desorption constant (i.e. $K_{ads}^A/K_{des}^A < 1$), only a small fraction of the maximum surface coverage is occupied by A prior to the start of the experiment. During the oxidation sweep, θ_A undergoes oxidation to form θ_B and the equilibrium position between the concentration adjacent to the electrode $C_{A,0}$ and the coverage θ_A is perturbed. The rapid depletion of the pre-adsorbed θ_A “out runs” the rate of adsorption and mass transport of A which results in a peak on the oxidative sweep. The decay of flux is a result of the total

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sites being occupied by adsorbed B. At higher K_{ads}^A the peak shape becomes narrower and occurs at lower potential with a quicker decay of flux; this is due to the higher fraction of total surface site $\theta_{A,pre-adsorbed}$ prior to the experiment.

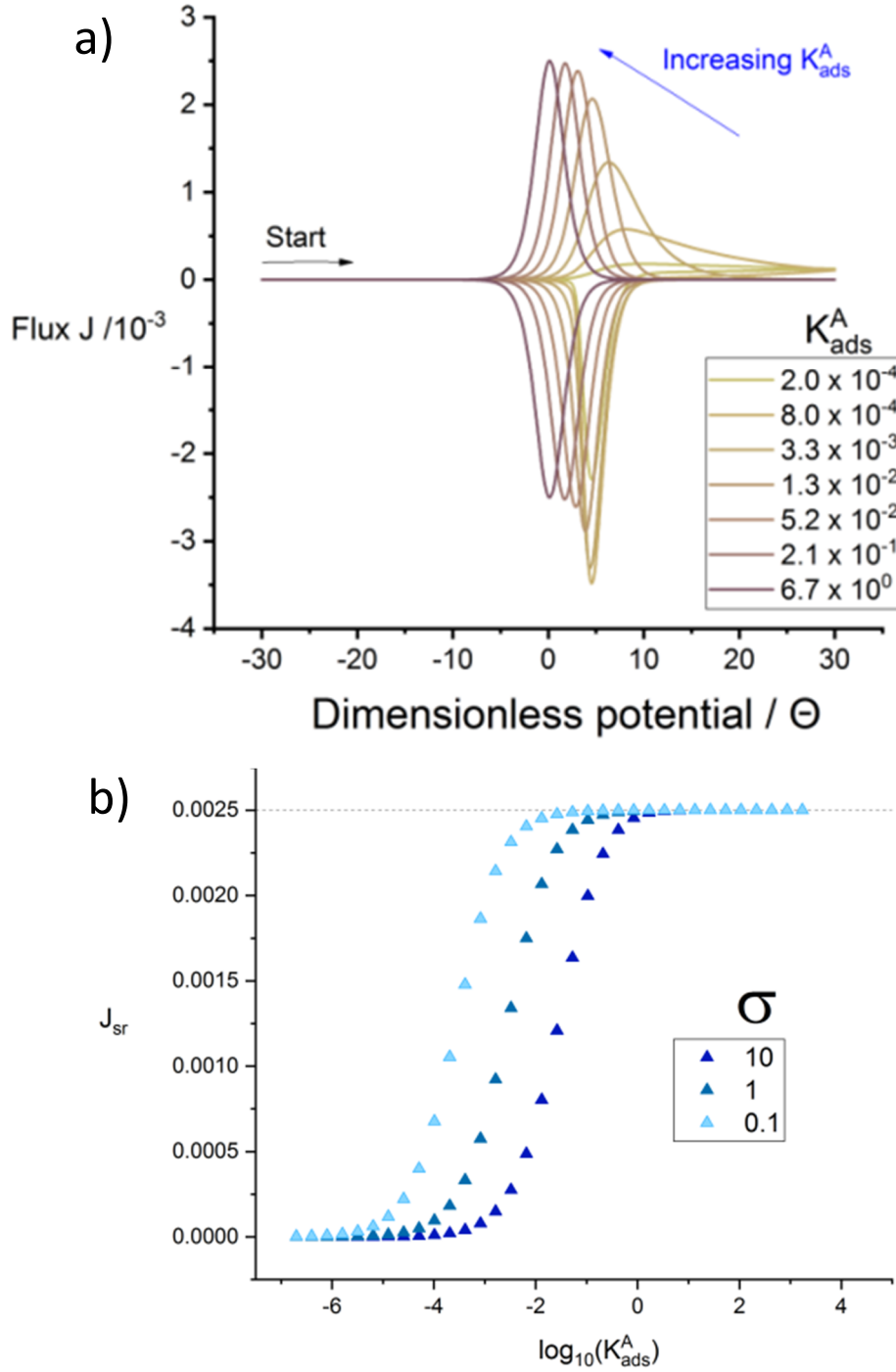


Figure 6.3. a) Simulated voltammograms of Limiting Case One with different adsorption rate constant of A, K_{ads}^A , under fast electron transfer kinetics $K_0 = 1 \times 10^7$ and $\sigma = 1$. b) plot of J_{sr} against the $\log(K_{ads}^A)$, where J_{sr} is the dimensionless peak flux J normalised against the dimensionless scan rate σ . Other parameters are: $B = 100$, $E_f^0 = 0$, $K_{des}^A = 1$, $K_{ads}^B = 0$, $K_{des}^B = 0$ and $d_B = 1$.

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In the limit of very large adsorption rate constant ($K_{ads}^A/K_{des}^A \gg 1$), the fraction of the pre-adsorbed surface coverage $\theta_{A,pre-adsorbed}$ approaches unity. The shape of the simulated voltammogram becomes symmetric with a peak flux J equal to 2.5×10^{-3} under the simulation condition of $\sigma = 1$ and $B = 100$. Since the formed product θ_B does not diffuse into solution in this case and all the adsorption sites were initially occupied by A, the simulated voltammogram matches exactly to that of a reversible surface-bound redox system.⁴⁷ The latter can be solved analytically to give an expression for the peak current, $\frac{n^2 F^2 \nu}{4RT} A \Gamma_{max}$, where n is the number of electron transferred and A is the area of the electrode; in the dimensionless form, the expression of peak flux J_{peak} for a fully reversible surface-bound system is $\sigma/4B$, which is in excellent agreement with the simulation result at large K_{ads}^A . Figure 6.3 b) shows a plot of the simulated peak flux for different scan rate σ , where J_{sr} is the normalised peak flux J_{peak} against scan rate σ . For all simulated σ , the J_{sr} approaches to $1/4B$ at high K_{ads}^A .

The simulated cyclic voltammogram for Case One with *slow* electron transfer kinetics, relative to mass transport, is shown in Figure 6.4 a). In contrast to Case One (fast electron transfer kinetics), the peak-to-peak separation increases due to an over-potential are needed to drive the sluggish electron transfer kinetics. As the adsorption rate constant increases relative to that of desorption, K_{ads}^A/K_{des}^A , the peak shape becomes narrower and similar to what was observed for *fast* electron transfer kinetics. Shown in Figure 6.4 b) is the plot of J_{sr} for different σ under *slow* electron transfer kinetics. In the limit of high K_{ads}^A , the peak flux J approaches 1.84×10^{-3} , which is lower compared to the value of 2.5×10^{-3} simulated under fast electron transfer kinetics. This limiting result of 1.84×10^{-3} can be derived analytically by considering as $K_{ads}^A \rightarrow \infty$, all the adsorption

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sites were occupied by A initially with no adsorption during the cyclic voltammetric simulation; therefore, the rate of consumption of θ_A under irreversible electron transfer kinetics is described by

$$\frac{\partial \theta_A}{\partial T} = -K_{ox} \theta_A, \quad \text{where } \theta_{A,pre-adsorbed} = 1, \quad K_{ox} = K_0 e^{\beta \theta} \text{ and } \theta = \theta_{initial} + \sigma T$$

(Eq. 6.27)

where θ is the applied potential and $\theta_{initial}$ is the applied potential at the start of the simulation. Solving this with the boundary condition leads to an expression of the surface coverage θ_A as a function of time T which gives the analytical solution for the peak flux $J = \frac{\beta \sigma}{B} e^{-1}$ (see Section 6.2.4 for derivation), which is in excellent agreement with the simulated result.

Overall and to summarize, Limiting Case One describes how K_0 , K_{ads}^A and σ varies the shape and peak flux of the voltammogram for when species B remains adsorbed. Next, Limiting Cases Two and Three builds upon Case One and investigate the simulated voltammograms in the scenario where the surface-bound $B(ads)$ can creep into the solution and diffuse away.

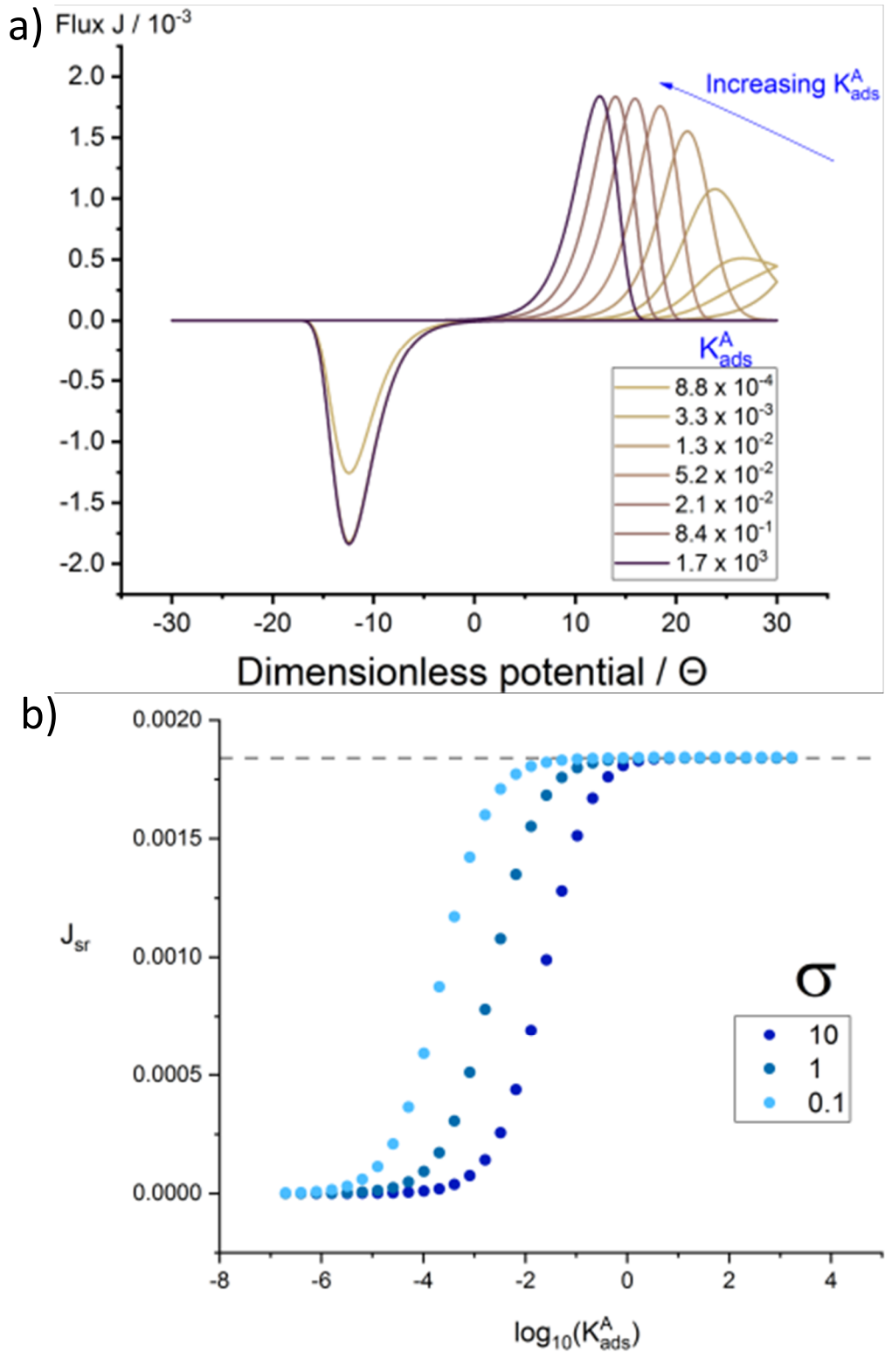


Figure 6.4. a) Simulated voltammograms of Limiting Case One with different adsorption rate constant of A , K^A_{ads} , under slow electron transfer kinetics $K_0 = 1 \times 10^{-3}$ and $\sigma = 1$. b) plot of J_{sr} against the $\log(K^A_{ads})$, where J_{sr} is the dimensionless peak flux J normalised against the dimensionless scan rate σ . Other parameters are: $\beta = 0.5$, $B = 100$, $E_f^0 = 0$, $K^A_{des} = 1$, $K^B_{ads} = 0$, $K^B_{des} = 0$ and $d_B = 1$.

6.3.2 Case Two – Species B is Partly Released into Solution

In Case Two, the model includes non-zero adsorption and desorption rate constants for species B . The schematic of Case Two is shown in Figure 6.5. Usually but not essentially the rate of desorption of B is set lower than the adsorption of B , $K_{des}^B < K_{ads}^B$. This allows the formed redox product θ_B to partially desorb into solution. Herein, the effect of varying K_0 , K_{ads}^A and K_{des}^B on the voltammogram will be investigated. The other parameters are set constant: $K_{des}^A = 1$, $K_{ads}^B = 1$, $d_B = 1$, $\sigma = 1$, $\beta = 0.5$ and $B = 100$.

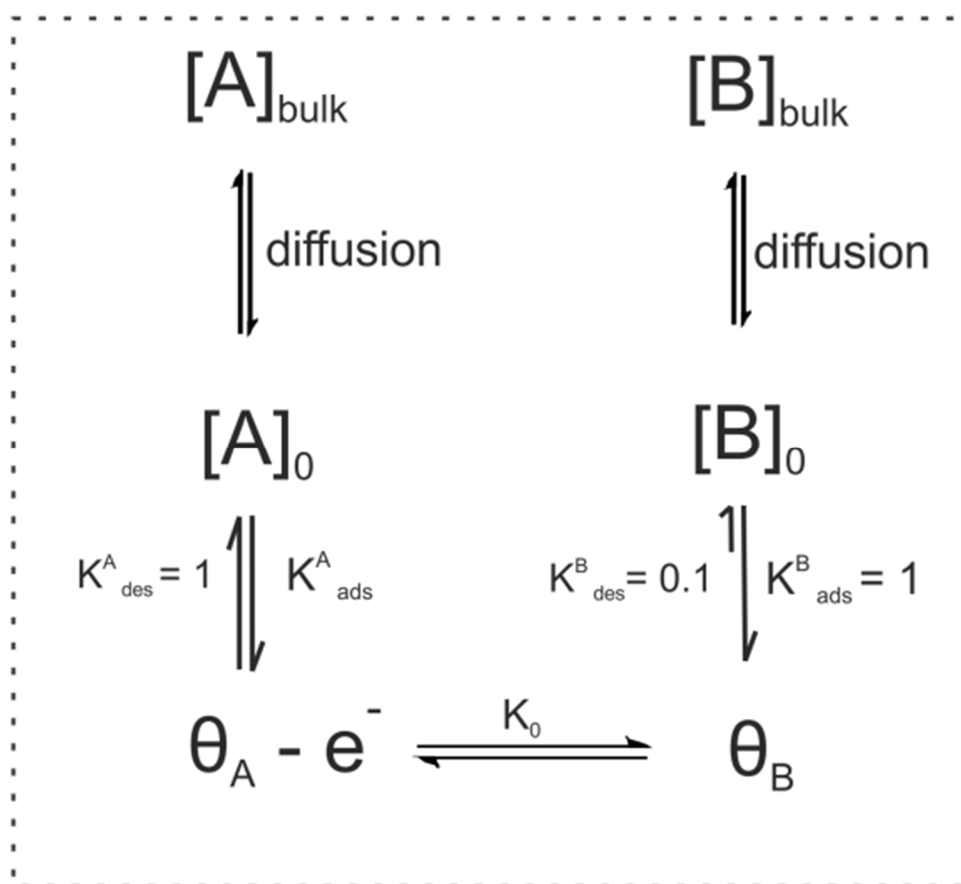


Figure 6.5. The reaction mechanism for Case Two, where some B slowly diffuses away from the electrode surface.

Figure 6.6 a) shows the cyclic voltammograms of Case Two under *fast* surface electron transfer kinetics with different adsorption rate constants for A , K_{ads}^A . At a slow K_{ads}^A , an oxidation peak appears on the forward sweep followed by a decay of current. As K_{ads}^A increases, the shape of the simulated voltammogram approaches a steady-state flux. A

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peak appears at slow K_{ads}^A due to the fast consumption of the pre-adsorbed θ_A with a gradual decay of flux from the interplay between the rate of adsorption of A , mass transport and the decreasing number of unoccupied sites on the electrode.

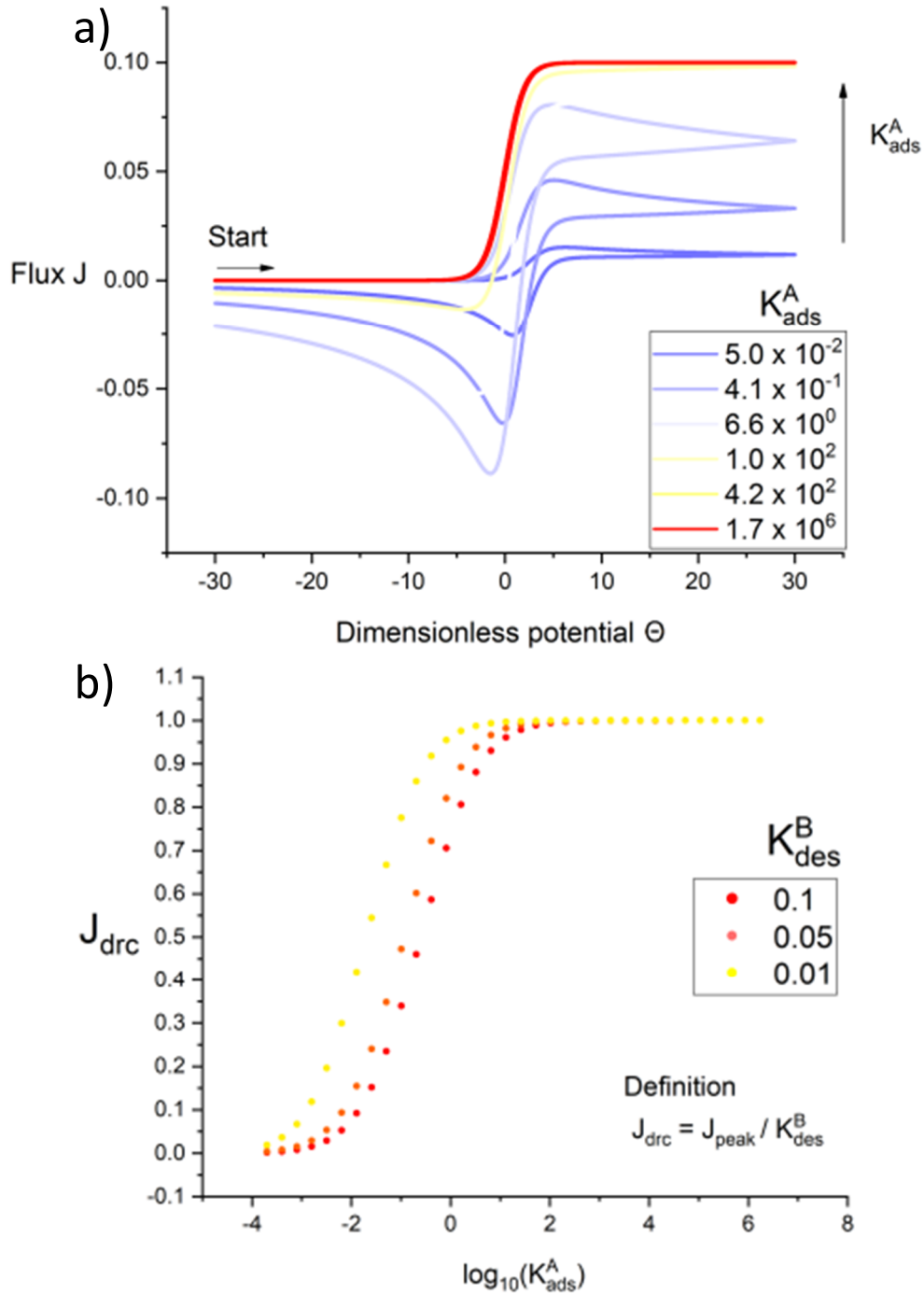


Figure 6.6. a) Simulated cyclic voltammogram of Case Two with increasing adsorption rate constant of A , K_{ads}^A , under fast electron transfer kinetics $K_0 = 1 \times 10^7$ and $K_{des}^B = 0.1$. b) Plot of J_{drc} against $\log(K_{ads}^A)$ under fast electron transfer kinetics $K_0 = 1 \times 10^7$ for different K_{des}^B . Other parameters are: $B = 100$, $\sigma = 1$, $E_f^0 = 0$, $K_{des}^A = 1$, $K_{ads}^B = 1$, and $d_B = 1$.

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Note the observed flux decay immediately after the oxidative peak is prolonged in Case Two, in contrast to Case One, due to the inclusion of the desorption of B which allows more A to be reduced. Figure 6.6 b) shows a plot of normalized peak flux J_{drc} as a function of K_{ads}^A for different magnitude of the desorption rate constant K_{des}^B

$$J_{drc} = J/K_{des}^B \quad (Eq. 6.28)$$

where J_{drc} is the peak flux J normalised against the desorption rate constant K_{des}^B . As the adsorption rate constant of A is larger than the desorption rate constant of B , $K_{ads}^A \gg K_{des}^B$, the flux becomes “bottlenecked” by the slow rate of desorption of B at overpotential. Under these conditions, the rate of desorption of B is equal to $K_{des}^B \theta_B$ and the flux J approximately equals to the desorption rate constant K_{des}^B (where $\theta_B \approx 1$). Therefore, J_{drc} in Figure 6.6 b) approaches unity when $K_{ads}^A \gg K_{des}^B$.

Next, the effect of *slow* electron transfer kinetics on Case Two is investigated; simulated voltammograms are shown in Figure 6.7 a). On the forward oxidation sweep, the peak shape resembles that under *fast* rates of electron transfer. However, the peak position shifts positively as the slower electron transfer kinetics requires a high overpotential to drive the current. Figure 6.7 b) plots the simulated peak flux J_{drc} against K_{ads}^A . As observed under *fast* electron transfer kinetics, the J_{drc} approaches unity at high K_{ads}^A as the desorption of B becomes the rate limiting step.

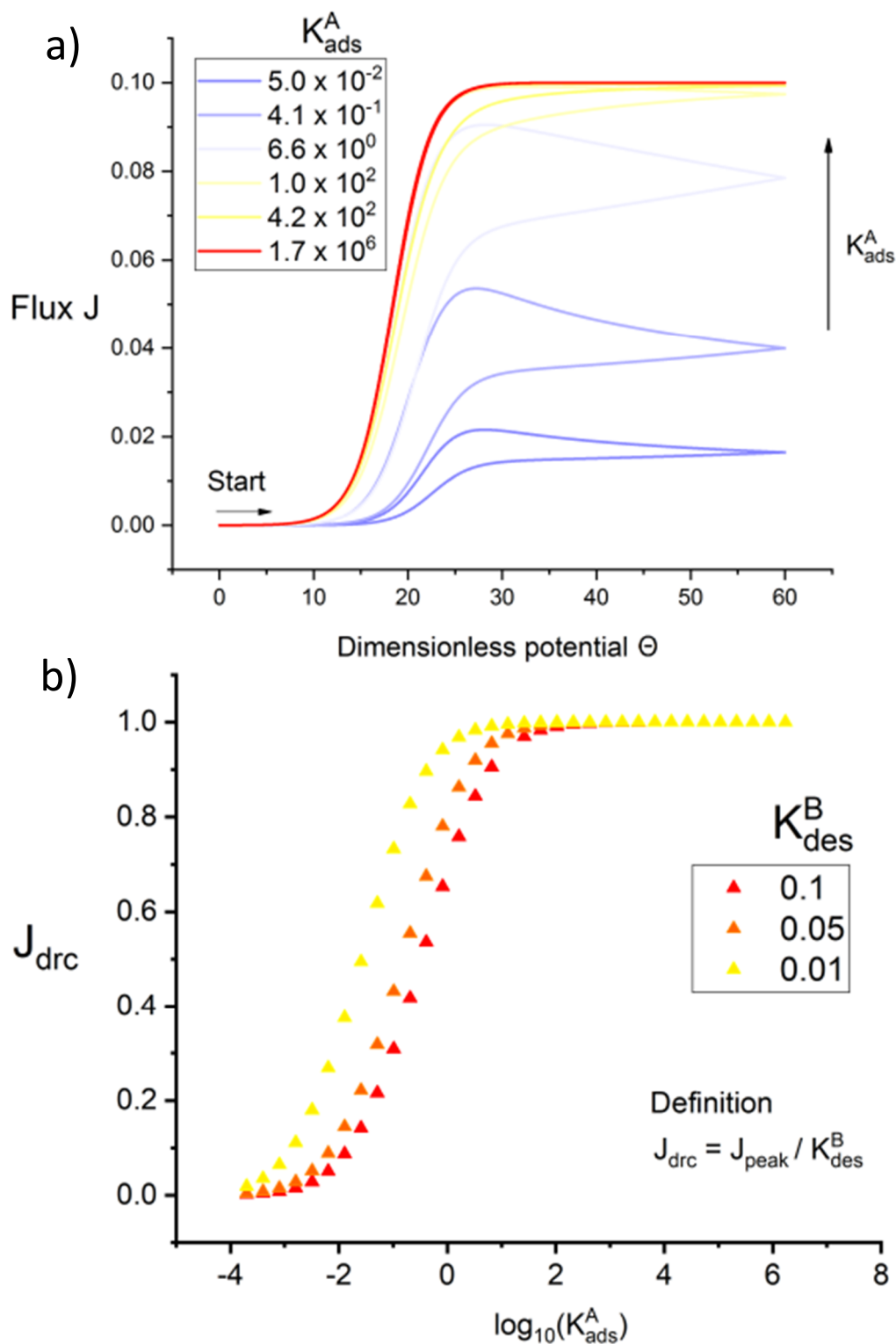


Figure 6.7. a) Simulated cyclic voltammogram of Case Two with increasing adsorption rate constant of A, K_{ads}^A , under slow electron transfer kinetics $K_0 = 1 \times 10^{-3}$ and $K_{des}^B = 0.1$. b) Plot of J_{drc} against $\log(K_{ads}^A)$ under slow kinetics $K_0 = 1 \times 10^{-3}$ for different K_{des}^B . Other parameters are: $B = 100$, $\sigma = 1$, $E_f^0 = 0$, $K_{des}^A = 1$, $K_{ads}^B = 1$, and $d_B = 1$.

In summary, interesting phenomena emerge from Case Two when $K_{ads}^A \gg K_{des}^B$. In this case, the shape of voltammogram reaches a steady-state current - the size of which reflects the rate of desorption of B . The next section will discuss the simulation results for the Limiting Case Three where, different from Case Two, the formed redox product θ_B desorbs *rapidly* into the bulk solution.

6.3.3 Case Three – Species B is Substantially Released into Solution

In Case Three, the formed redox product θ_B is allowed to desorb quickly into solution. The reaction mechanism is illustrated in Figure 6.8. The effect of K_{ads}^A , K_0 and σ on the voltammetric shape and peak flux is considered. Other parameters were set constant: $K_{des}^A = 1$, $K_{des}^B = 1 \times 10^6$, $K_{ads}^B = 1$, $d_B = 1$, $\beta = 0.5$ and $B = 100$.

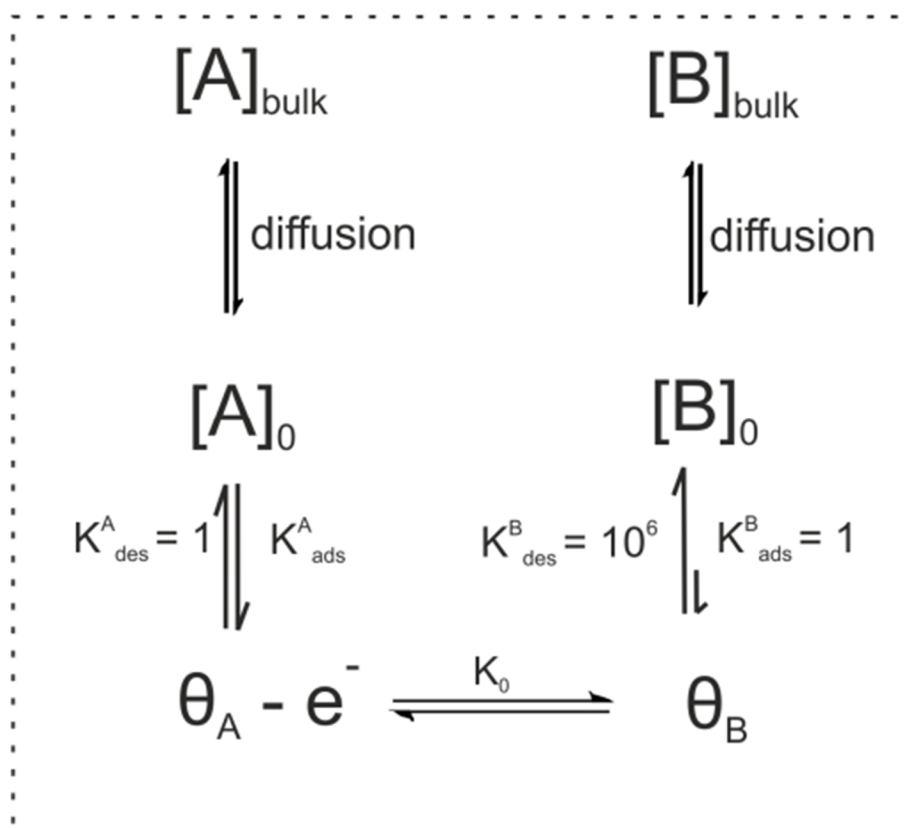


Figure 6.8. The reaction mechanism for Case Three, where the adsorbed species B desorbs rapidly after formation.

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The voltammograms of Case Three were simulated under *fast* electron transfer kinetics for different K_{ads}^A , shown in Figure 6.9 a). The oxidative peak potentials shift negatively due to the rapid desorption of the formed redox product which drives the reaction at low potentials. Interesting, as K_{ads}^A increases, the oxidative peak shape becomes narrower. As the rate of adsorption of A increases to a magnitude comparable to the rapid desorption of B ($K_{ads}^A \approx K_{des}^B = 1 \times 10^6$), the flux J increases sharply on the oxidative sweep before a sudden and rapid decay that leads to a sharp oxidative wave. This is similar to that observed for the voltammograms simulated under *slow* electron transfer kinetics, shown in Figure 6.10 a). In the limit of a rapid rate of adsorption of A and desorption of B , the limiting step in the system becomes the rate of electron transfer and the mass transport of material from the bulk solution.

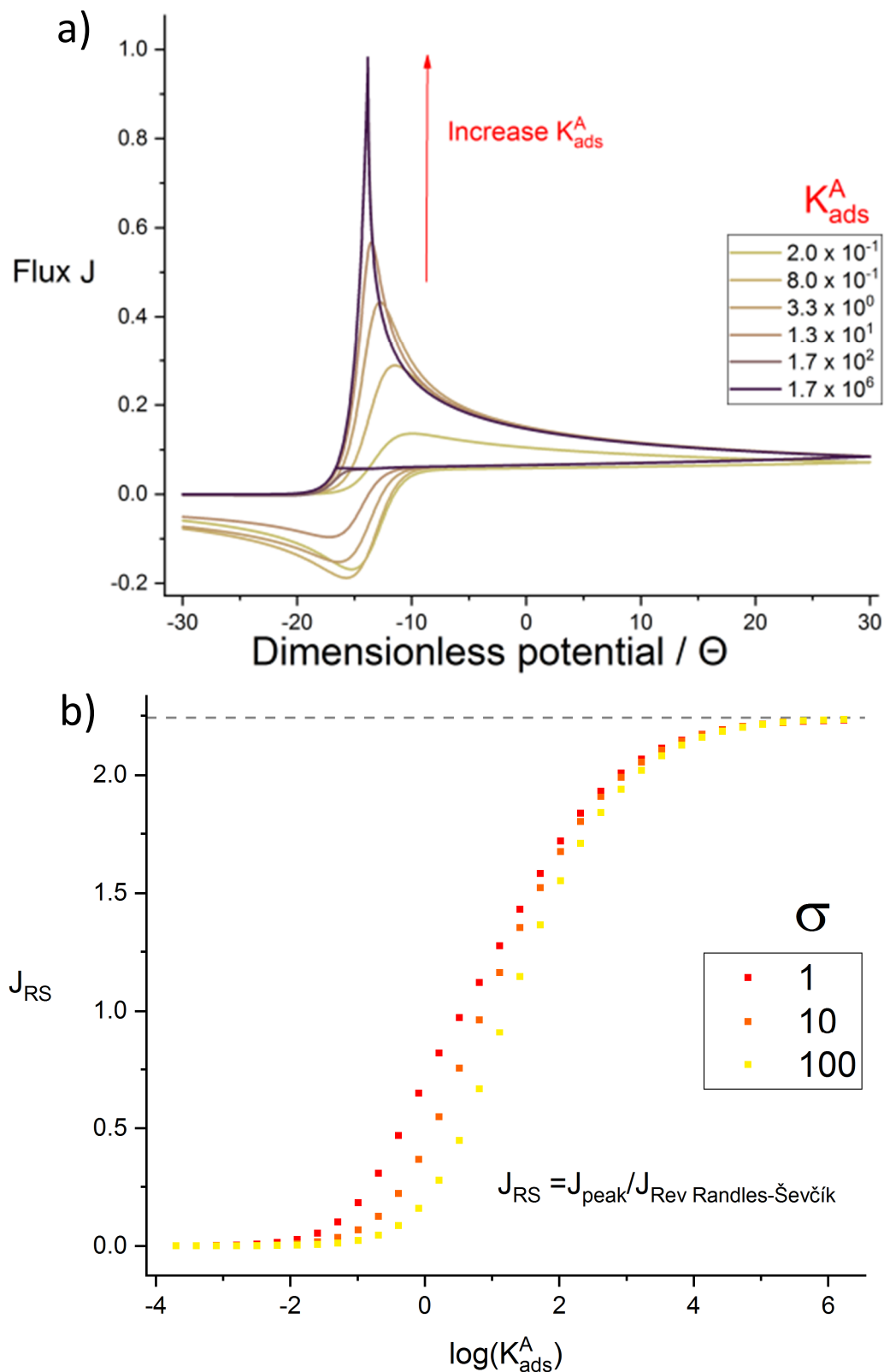


Figure 6.9. a) Simulated cyclic voltammogram of Case Three with increasing adsorption rate constant of A , K_{ads}^A , under fast electron transfer kinetics $K_0 = 1 \times 10^7$ and $\sigma = 1$. b) Plot of J_{RS} against $\log(K_{ads}^A)$ under fast kinetics $K_0 = 1 \times 10^7$ for different σ . Other parameters are: $B = 100$, $E_f^0 = 0$, $K_{des}^A = 1$, $K_{ads}^B = 1$, $K_{des}^B = 1 \times 10^6$ and $d_B = 1$.

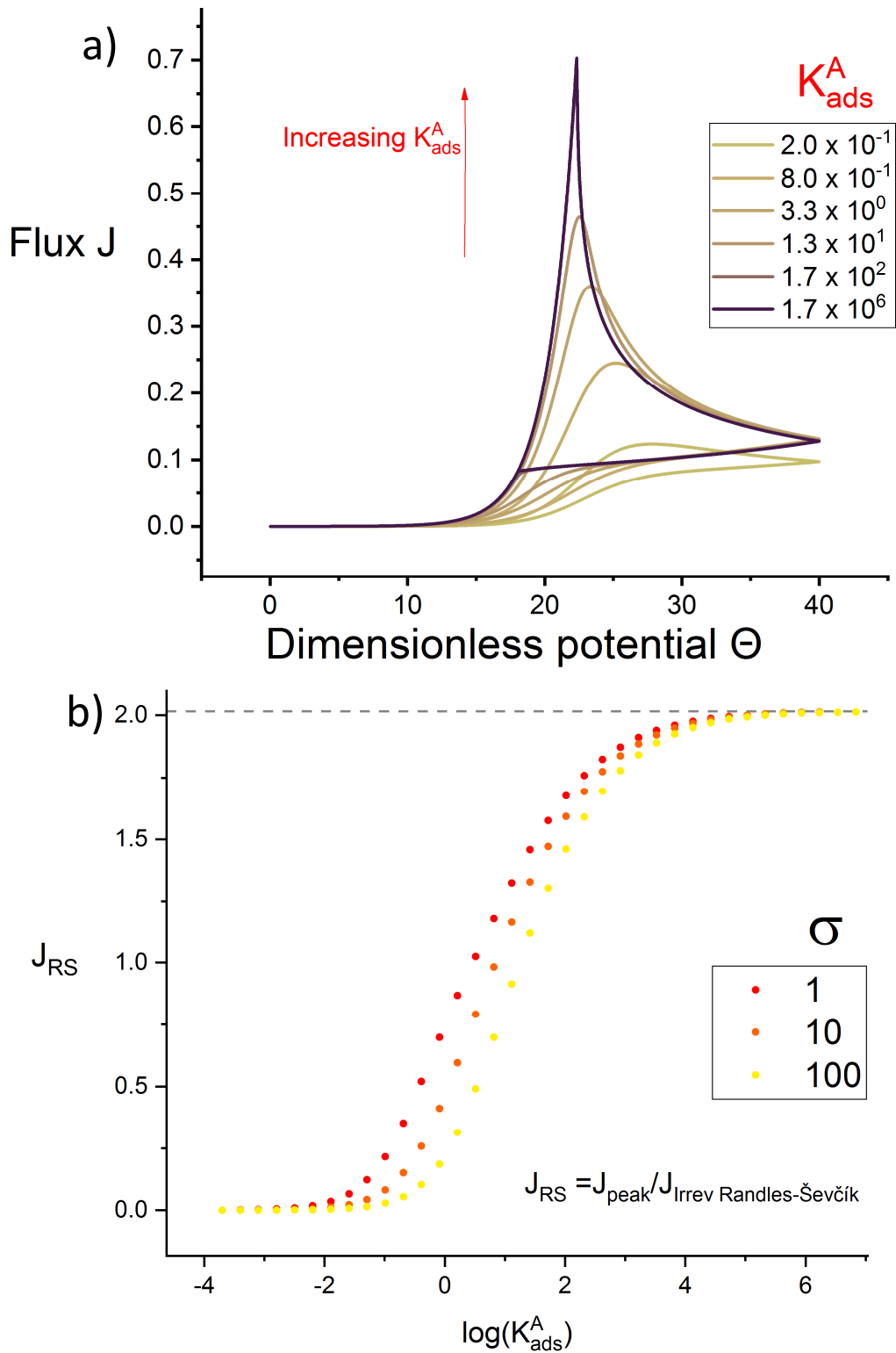


Figure 6.10. a) Simulated cyclic voltammogram of limiting Case Three with increasing adsorption rate constant of A, K_{ads}^A , under slow electron transfer kinetics $K_0 = 1 \times 10^{-3}$ and $\sigma = 1$. b) Plot of J_{RS} against $\log(K_{ads}^A)$ under slow kinetics $K_0 = 1 \times 10^{-3}$ for different σ . Other parameters are: $B = 100$, $E_f^0 = 0$, $K_{des}^A = 1$, $K_{ads}^B = 1$, $K_{des}^B = 1 \times 10^6$ and $d_B = 1$.

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The simulated peak fluxes may be insightfully compared and contrasted to that for a simple solution-phase redox system, $A_{(aq)} - e^- \rightleftharpoons B_{(aq)}$, where the electron transfer occurs from the solution phase with the peak currents described by the Randles-Ševčík equation.^{50, 51} This leads to the normalization of

$$J_{RS} = J_{peak}/J_{Randles - \check{S}ev\check{c}ik} \quad (Eq. 6.29)$$

where the dimensionless form of the Randles-Ševčík equation in the limit of a fully reversible or fully irreversible electron transfer kinetics can be written as

$$J_{rev,Randles - \check{S}ev\check{c}ik} = 0.446\sqrt{\sigma} \quad (reversible)$$

$$J_{irrev,Randles - \check{S}ev\check{c}ik} = 0.496\sqrt{\beta\sigma} \quad (irreversible) \quad (Eq. 6.30)$$

Figure 6.9 b) and Figure 6.10 b) shows a plot of J_{RS} as a function of K_{ads}^A and σ . Interestingly, for both reversible and irreversible electron transfer kinetics, J_{RS} can exceed unity as K_{ads}^A increases with the former approaches to a value of $1/0.446$ and the latter to $1/0.496$ – these values are independent of the saturation parameter B for the scan rates investigated. Note, this is **not** due to the flux contribution from the pre-adsorbed $A(ads)$, since as seen in Case One, the dimensionless peak flux from a pre-adsorbed monolayer of A is 2.5×10^{-3} for the reversible and 1.8×10^{-3} for irreversible electron transfer kinetics. This is almost three orders of magnitude smaller than that observed for Case Three, hence the unexpected result of J_{RS} exceeding unity arises solely from mass transport effects from the bulk solution.

To understand the origin of the sharp peak shape and the discrepancy with the Randles - Ševčík equation, we consider the calculation of the flux J for both cases. For a redox couple that undergoes electron transfer without the need to adsorb, the flux of electrons $J_{solution\ phase}$ is a function of the surface concentrations and the rate of electron transfer, described by the Butler-Volmer equation:

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$$J_{\text{solution phase}} = K_{\text{ox}}C_{A,0} - K_{\text{red}}C_{B,0} \quad (\text{Eq. 6.31})$$

where $C_{A,0}$ and $C_{B,0}$ is the concentration of species A and B at the electrode surface, respectively. For simplification, we will discuss the fully irreversible case where the rate of the backward reaction K_{red} is negligible. Under irreversible electron transfer kinetics, $J_{\text{solution phase}}$ is the product of K_{ox} and $C_{A,0}$. During the oxidative sweep, the rate of oxidation K_{ox} increases exponentially with the applied potential but the surface concentration of A is consumed during this process to form B . In contrast, the flux J in the adsorption model under irreversible electron transfer kinetics is the product of K_{ox} and θ_A . From the adsorption model, in the limit of $K_{\text{ads}}^A \rightarrow \infty$, the oxidative wave peaks at a dimensionless potential θ of 22.3; the surface coverage of A and B , and the concentration profile of A in solution are plotted in Figure 6.11 a) and b) respectively. The time axis in Figure 6.11 is normalized to the simulation duration, where the oxidation peak potential θ_{peak} occur at a dimensionless time T of 0.27. The plot of surface coverage shows that θ_A is maintained at unity from the start of the simulation up until $T = 0.27$, which is the moment when the surface concentration $C_{A,0}$ depletes to zero. Thus the exponential increase in flux J during the oxidation sweep at high K_{ads}^A is the result of θ_A maintained at unity until the depletion of $C_{A,0}$. Figure 6.12 shows the simulated CV of Case Three with K_{ads}^A equal to 1.7×10^6 under irreversible electron transfer kinetics. The exponential increase in flux is in excellent agreement with the calculated K_{ox} as a function of the dimensionless potentials θ , overlaid as circles. Thus, in the limit of high K_{ads}^A and K_{des}^B , a redox couple that undergoes electron transfer via adsorption can result a peak current ca. 2.3 times larger than that undergoes electron transfer in the solution phase; a surprising but impactful result from the simulation.

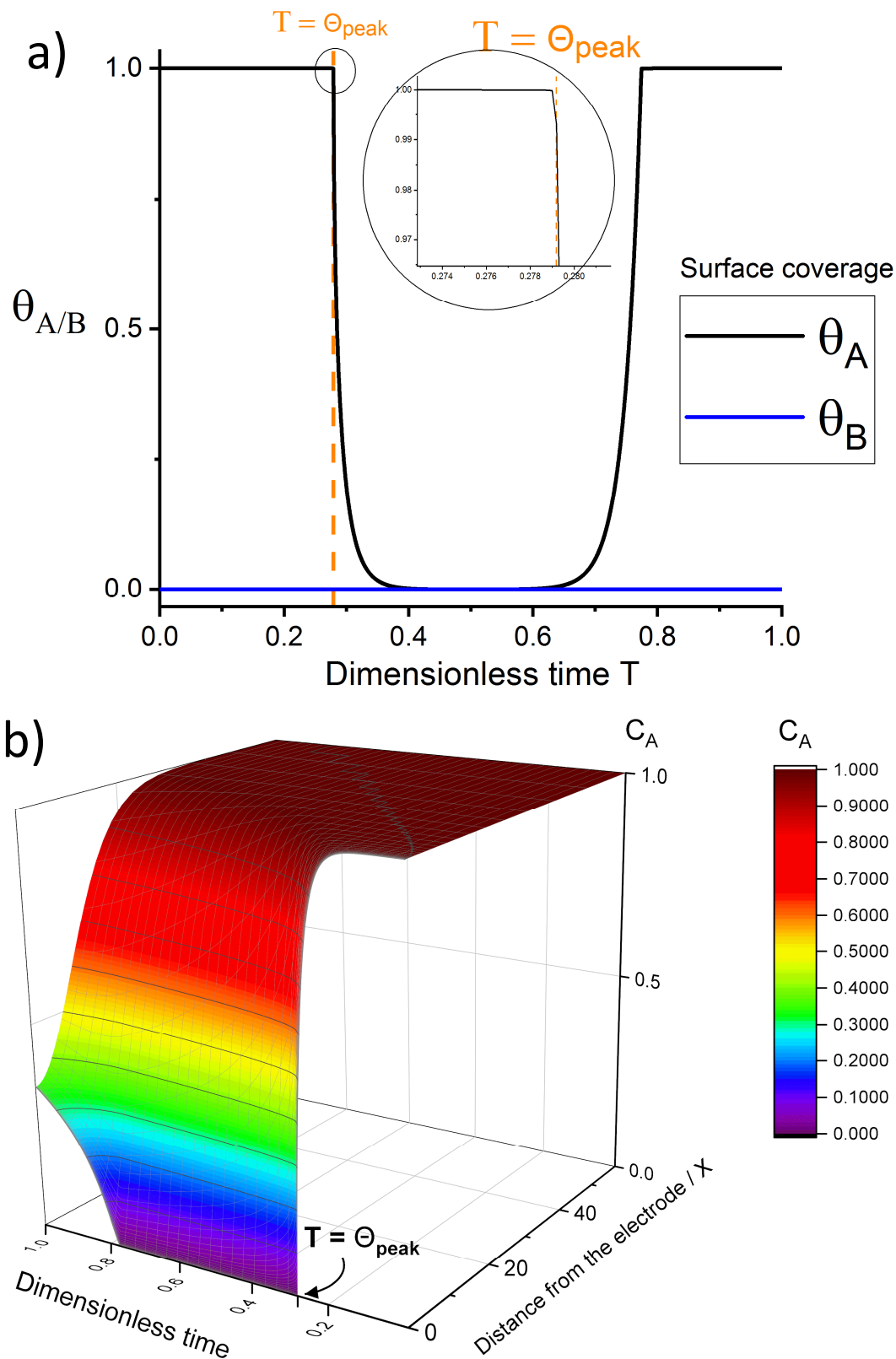


Figure 6.11. a) The surface coverage profile of A and B, and b) concentration profile of A. Both plots were obtained during the simulation of Case Three under irreversible kinetics and $K_{ads}^A = 1.7 \times 10^6$. Other parameters are: $B = 100$, $E_f^0 = 0$, $K_{des}^A = 1.7 \times 10^6$, $K_{ads}^B = 1$, $K_{des}^B = 1$ and $d_B = 1$.

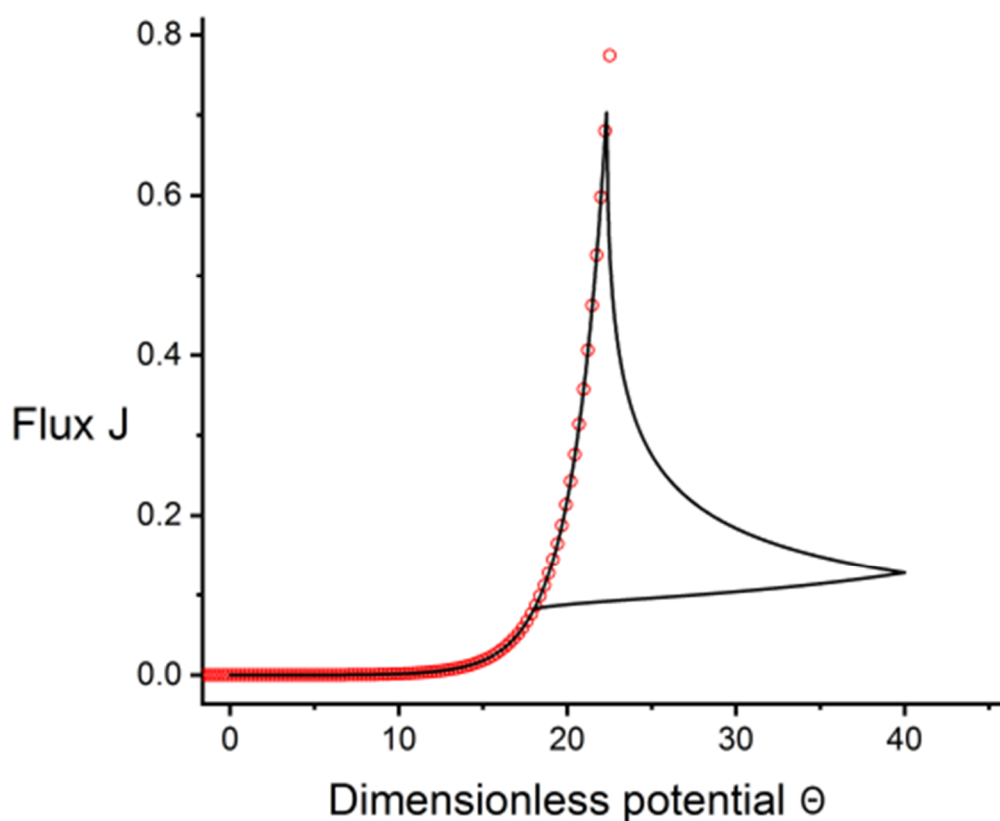


Figure 6.12. Black line - the simulated cyclic voltammogram for Case Three under irreversible kinetics and $K_{ads}^A = 1.7 \times 10^6$. Red circles – calculated values of K_{ox} as a function of dimensionless potential Θ .

6.3.4 Diagnosis of Different Limiting Adsorption Cases: a Summary

The voltammetric shape and peak current in the three cases discussed above, in which the extent of product desorption differs, are distinctively different for each of the scenarios. Simulated voltammograms can be used to identify different limiting adsorption cases from experiments. In Case One, the product remains on the surface and results in a symmetric peak shape, characteristic of surface-bound voltammetry. In Case Two, when desorption of the product becomes the rate-determining step, the current approaches an apparent steady-state. In Case Three, the voltammetric shape is abnormally sharp when the adsorption kinetics are fast and not rate-determining; the resulting flux can be up to 2.3 times bigger in contrast to electron transfer that occurs in the solution phase. In

addition, the saturation parameter B is a function of the bulk concentration of the reactant allowing easy control over the parameters with the possibility that a change of concentration in the experiment may lead to a switch to a different adsorption mechanism.

6.4 Conclusions

The adsorption model in this Chapter provides new insights to the voltammetric behaviors of surface-bound redox systems. The developed model embraces all of adsorption kinetics, mass transport and electron transfer kinetics of the reactant and products; under certain conditions, this leads to a number of interesting hitherto unexpected current-voltage responses. Most noticeably, the one-dimensional simulation for a macro-electrode reaches a steady-state current when rate-determining step becomes ‘bottlenecked’ by the slow desorption of the product. Furthermore, when the rate of adsorption and desorption of the reaction and product are fast and not rate-determining, the simulated current for the redox process via the adsorption pathway can be ca. 2.3 times higher to that when electron transfer occurs via the solution phase.

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Chapter 7 Voltammetry of Adsorbed Species: Non-ideal Interactions Leading to Phase Transitions

This Chapter continues the simulation work discussed in Chapter 6 where the voltammetric responses which arise due to different adsorption pathways were simulated. The work herein focus on the effects of surface interaction for one specific redox mechanism, the electro-sorption reaction $A(aq) + e^- \rightleftharpoons B(ads)$. This mechanistic pathway involves a solution phase species $A(aq)$, which upon transfer of an electron at the electrode interface, forms a surface-bound product $B(ads)$ that remains adsorbed up to a maximum of a monolayer. The adsorption/desorption and electron-transfer studied herein is a *concerted* process, different from the stepwise process as seen in Case One of Chapter 6. This bespoke reaction pathway is applicable to, almost exclusively, underpotential deposition metals on foreign surfaces, which is scientifically significant across all Physical Sciences and especially to applications in materials, catalysis and interfacial science.

The theory section of this Chapter first introduces the adsorption isotherm, developed by Frumkin, to account for the possible surface interactions such as those between adjacent surface-bound adsorbates. This isotherm is widely acknowledged for its success in explaining the experimental deviations from Langmuir isotherm when higher concentrations of adsorbate were used. Moreover, the Frumkin isotherm predicts that a phase-transition behaviour if the adsorbate-adsorbate interaction is strongly attractive – so the question arises as to whether is this possible for electro-sorption reactions, measured under voltammetric conditions? Similarly what are the voltammetric responses

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when the adsorbate-adsorbate interaction deviates from ideality, i.e. with overall, net attractive or repulsive forces? And to what extent does mass transport affect the voltammetric signal? The simulation work presented in this Chapter seeks to provide new insights to the above-posed questions.

The results presented in this Chapter were recently accepted for publication in the *The Journal of Physical Chemistry C*. Full reuse permission has been granted for the purpose of this thesis.¹

7.1 Introduction

The understanding of electrochemical interfaces significantly advanced during the twentieth century partly because of the extensive electrocapillary measurements made on a mercury-water interface in the presence of organic molecules.²⁻⁴ The most notable contributor in this area was Alexander N. Frumkin, a Soviet electrochemist who contributed remarkably in this field and is widely known as the ‘father of modern electrochemistry’ for his pioneering work.⁵ One of his most recognised works include the development of an adsorption isotherm, bearing his name, to explain the experimental data obtained by him and his co-workers’ on the adsorption of various organic molecules on mercury by accounting for non-ideality arising from adsorbate-adsorbate interactions.⁶ Since then, a wide range of alternative adsorption isotherms have been developed with varying degrees of complexity⁷⁻⁹. Nevertheless, the adsorption isotherm developed by Frumkin remains one of the best in giving agreement with a diversity of large sets of experimental data.^{7, 10}

Accounting for surface interactions is vital for voltammetry involving adsorbed species as it plays a crucial role in the influencing both the thermodynamics and the rate of interfacial reactions. For a simple one-electron transfer redox couple, either both, one or none of the reactant and product can be adsorbed on the electrode surface. As already discussed in Chapter 6, the simulation work for *both* species adsorbed was extensively studied by Laviron *et al.*, in which he incorporated the Frumkin isotherm to study the effect of lateral surface interactions.¹¹⁻¹³

Redox couples involving only *one* strongly adsorbed species (Equation 7.1) are common in a vast number of electrochemical processes covering a wide range of redox reactions.¹⁴⁻

¹⁶ In particular under-potential deposition (UPD) of metal atoms on a foreign surface leading to a monolayer of adatom is relevant across many scientific and technological

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disciplines involving materials, surface and catalysis scientific. Over recent decades, advances in the preparation of pristine single-crystal surfaces allow surface interactions to be studied on individual facets of the same electrode material. This includes, but is not limited to, under-potential deposition of the following adatom layers; H,¹⁷⁻¹⁹ Cu²⁰⁻²³ and Ag²⁴⁻²⁶ on Pt electrodes; Cu,²⁷⁻²⁹ Ag,³⁰⁻³² Pb³³⁻³⁵ and Hg³⁶⁻³⁸ on Au electrodes; Tl^{39, 40} and Pb⁴¹⁻⁴³ on Ag electrodes. Notice that, the formation of adatoms in UPD reactions, or in the more generally termed electro-sorption reactions in this Chapter (Equation 7.1), involves a single *concerted* step accompanying charge-transfer across the interface, different to that of the stepwise adsorption kinetics of the reactant followed by charge-transfer as seen in Chapter 6. Beyond the niche substrate of single-crystal surfaces, which are typically somewhat exclusively studied, UPD can occur with liquid mercury electrodes leading to the formation of HgS monolayers.⁴⁴⁻⁴⁶ It is not uncommon that UPD results in an abnormally narrow and sharp voltammetry peak,^{41, 42, 44} for example, a peak width as low as 3.2 mV was reported for the UPD of lead on Ag (111),⁴² in contrast to the ‘ideal’ 90 mV/*n* derived analytically for non-interacting adsorbates (*n* is the number of electrons transferred).⁴⁷⁻⁴⁹ To understand this, simulations accounting for surface interactions are necessary. The common approach to determine the magnitude of the surface interactions in the literature is to interpret the size of the peak width but the full waveshape is better diagnostic and informative. The mathematical problem to be solved is commonly simplified by assuming throughout a diffusionless system, i.e. $c_{A,0} = c_{A,bulk}$ where *c* is the solution phase concentration and the subscripts denote either the surface or bulk values, at all times, justified experimentally by the use of a high concentration of the reactant (0.1M) and extreme slow voltage scan rates (0.1 mVs⁻¹).^{42, 44, 49, 50} Of those few studies accounting for mass transport, Baranski *et al.* modelled the surface process as a transfer of the adsorbate from the Outer- to the Inner-Helmholtz

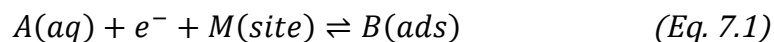
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Plane coupled with the Frumkin adsorption isotherm.⁵¹ whilst Fawcett *et al.* focused on the desorption process.⁵²

This Chapter simulates the voltammetry of an electro-sorption reaction involving one species strongly adsorbed on the electrode surface. The next section takes a bottom-up approach to develop the mathematical model coupling the Frumkin adsorption isotherm with Butler-Volmer kinetics to describe the surface electrode kinetics. The underlining physicochemical processes and effects of surface interactions are studied and, in particular, consider the strong interactions leading to phase transition behaviours in voltammetry. Moreover, this simulation work demonstrates that mass transport in the solution phase is, in fact, crucial in the interpretation of experimentally obtained voltammograms close to phase transitional surface interactions – even if a significant excess in solution concentrations and slow scan rates are deployed.

7.2 Theoretical Model

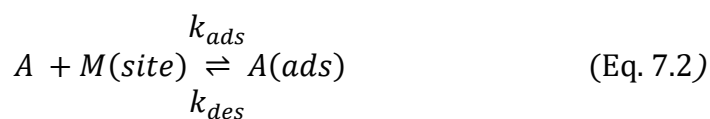
In the following a one-step electro-sorption reaction is considered



where a solution phase species $A(aq)$ gains an electron to form species $B(ads)$ adsorbed onto an unoccupied site on a macro-electrode. This section first discusses quite generally the adsorption isotherms which account for non-ideal surface interactions. Next, the electrode kinetics describing the heterogeneous rate constant as a function of the applied potential is developed for the case of Equation 7.1. This requires a bespoke formal potential E_f^0 to be defined, complementary to that adopted by IUPAC. Finally, a full mathematical model, including diffusional effects, for the simulation of the reaction in Equation 7.1 is outlined together with the definitions of the dimensionless parameters used to report results.

7.2.1 Adsorption Isotherms

First, we consider a general adsorption process where a species A, either in the gas phase or aqueous phase, adsorbs onto a surface with unoccupied equivalent sites $M(site)$ becoming surface-bound $A(ads)$



where k_{ads} is the adsorption rate constant ($\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$), k_{des} is the desorption rate constant (s^{-1}). In an ideal scenario, the adsorbates on the surface do not interact, all sites are identical and can only one adsorbate occupy one site. The rate of adsorption is then directly proportional to an adsorption rate constant k_{ads} , the interfacial concentration of $c_{A,0}$ and the number of unoccupied sites ($\Gamma_{max} - \Gamma_A$). Similarly, the rate of desorption

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will be directly proportional to the desorption rate constant k_{des} and the coverage of surface-bound A (Γ_A), giving rise to a general net rate law

$$rate = \frac{d\Gamma_A}{dt} = k_{ads}c_{A,0}(\Gamma_{max} - \Gamma_A) - k_{des}\Gamma_A \quad (Eq. 7.3)$$

where t is time (s), $c_{A,0}$ is the interfacial concentration of A (mol m^{-3}), Γ_{max} is the total number of sites on the surface (mol m^{-2}) and Γ_A is the coverage of the sites occupied by A (mol m^{-2}). When equilibrium between the surface and the bulk solution is established, the *net* rate of adsorption and desorption is zero, returning the Langmuir ideal adsorption isotherm⁵³

$$\frac{k_{ads}}{k_{des}}c_{A,0} = \frac{\theta}{1-\theta} \quad (Eq. 7.4)$$

where θ is the fractional surface coverage ($\frac{\Gamma_A}{\Gamma_{max}}$) and $c_{A,0}$ equals $c_{A,bulk}$ at system equilibrium. However, many aqueous soluble neutral organic compounds such as aliphatic oxygen compounds, amines and aromatics adsorb strongly onto electrodes, particularly the much-studied mercury electrode.^{54, 55} The surface interactions arising from, for example, dipole-dipole interactions between the neighbouring adsorbates⁵⁶⁻⁵⁸, and, in the case of aromatic compounds, π -electrons interaction with mercury electrode,⁵⁹⁻⁶¹ are far from negligible. In most cases, such as those classically observed in electrocapillary experiments on mercury, the net interaction on the surface is not zero. To account for these non-ideal surface interactions, Frumkin⁵ developed the adsorption isotherm bearing his name in 1926⁶²

$$\frac{k_{ads}}{k_{des}}c_{A,0} = \frac{\theta}{1-\theta} \exp(g\theta) \quad (Eq. 7.5)$$

where g is the “Frumkin adsorbate-adsorbate interaction parameter” and again, $c_{A,0}$ equals $c_{A,bulk}$ at equilibrium. Since the isotherm describes the surface coverage versus bulk concentration at equilibrium, the position of this equilibrium is necessarily

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controlled by the Gibb's energy of adsorption. One of the approximations leading to the derivation of the Frumkin isotherm is that the adsorbate-substrate interaction contributing to the Gibb's energy of adsorption ($\Delta G_{\theta}^{\circ}$) is independent of the coverage of adsorbate, but that arising from adsorbate-adsorbate interactions, is however, dependent and assumed to vary linearly with coverage ($\Delta G_{\theta}^{\circ} = \Delta G_{\theta=0}^{\circ} - g\theta$).^{48, 63} In this Chapter, the term non-ideal surface interaction refers to a non-zero adsorbate-adsorbate interaction parameter g , which could either be positive or negative. A positive g indicates repulsion between the surface-bound species and a negative g indicate attractive forces. Note, the Langmuir ideal adsorption isotherm is a special case of Frumkin's adsorption isotherm when g equals zero. It can be seen from the adsorption isotherm that when g is small, and the contribution from the exponential term is low, the fractional surface coverage θ at equilibrium will increase with $c_{A,bulk}$; however, when the surface interaction is strongly attractive ($g \leq -4$), the plot of θ vs $c_{A,bulk}$ becomes less intuitive with indications of phase transition like behaviour, of which more below.² The adsorption-desorption rate law accounting for the non-ideal interactions underpinning the Frumkin isotherm is^{51, 52}

$$rate = \frac{d\Gamma_A}{dt} = k_{ads}c_{A,0}(\Gamma_{max} - \Gamma_A)\exp(-g^{\ddagger}\theta) - k_{des}\Gamma_A \exp((g - g^{\ddagger})\theta) \quad (Eq. 7.6)$$

where the additional term $g^{\ddagger}$ is introduced to account for the lateral interactions between the activated complex (transition state) and adsorbed molecules.

7.2.2 Electrode Kinetics

For surface redox processes, the electrode kinetics can be successfully accounted for by the asymmetric Marcus-Hush theory involving a 're-organisation energy' and an asymmetry factor.⁶⁴⁻⁶⁶ For small over-potentials, however, where the Tafel slope is typically linear the rates can be described by the semi-empirical Butler-Volmer

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kinetics.⁶⁷⁻⁶⁹ For a simple one-electron process $A(aq) \pm e^- \rightleftharpoons B(aq)$ this gives simple expressions for the electron transfer rate constants k_{ox} for oxidation and k_{red} for reduction. These vary exponentially with the applied potential E and depend on a transfer coefficient α

$$k_{red} \propto e^{-\frac{\alpha F}{RT}(E)} \text{ and } k_{ox} \propto e^{\frac{(1-\alpha)F}{RT}(E)} \quad (Eq. 7.7)$$

where T is the temperature (K), R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$) and F is the Faraday constant ($96485.3 \text{ C mol}^{-1}$). For a fully aqueous phase redox couple with a formal potential E_f^0 as defined by the IUPAC (Section 7.2.3), the Butler-Volmer kinetics is more conveniently and thus commonly expressed relative to the standard formal potential $(E - E_f^0)$ giving rise to

$$k_{red} = k_0 e^{-\frac{\alpha F}{RT}(E - E_f^0)} \text{ and } k_{ox} = k_0 e^{\frac{(1-\alpha)F}{RT}(E - E_f^0)} \quad (Eq. 7.8)$$

where k_0 is the standard electrochemical rate constant. An adapted form of Butler-Volmer kinetics is used here for ease of computation and because it allows exploration of non-ideal surface interactions coupled with mass transport.

Specifically, Butler-Volmer kinetics here is coupled into the adsorption-desorption rate law accounting for non-ideal surface interactions leading to the following expression for the adsorption flux of A at the electrode interface^{51, 52, 70}

$$D_A \left(\frac{\partial c_A}{\partial x} \right)_{x=0} = k'_{red} c_{A,0} (\Gamma_{max} - \Gamma_B) \exp(-g^\ddagger \theta_B) - k'_{ox} \Gamma_B \exp((g - g^\ddagger) \theta_B) \quad (Eq. 7.9)$$

where D_A is the diffusion coefficient of species A, k'_{red} ($\text{m}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and k'_{ox} (s^{-1}) are the electro-sorption rate constants for the electro-adsorption and electro-desorption reaction, respectively. Herein, an apostrophe is used to differentiate electro-sorption rate

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constants from the usual electron transfer rate constants. The former, analogous to Butler-Volmer kinetics, are exponentially dependent on the applied potential E

$$k'_{red} = k''_{red} e^{-\frac{\alpha F}{RT}(E)} \quad (Eq. 7.10)$$

$$k'_{ox} = k''_{ox} e^{\frac{(1-\alpha)F}{RT}(E)} \quad (Eq. 7.11)$$

where $k''_{red/ox}$ are the pre-exponential constants. It is, however, more insightful to express k'_{red} and k'_{ox} in terms of an applied potential relative to a suitably defined formal potential.

7.2.3 Definition of the Formal Potential E_f^0

The definition of formal potential as adopted by IUPAC is as follows “[The] Conditional (formal) potential, $E_c^{0'}$, is related to the potential of a cell reaction, E_{cell} , by an equation analogous to that relating E_{cell} to the standard potential E_0 , with the activity, a_i , replaced by any composition variable, c_i (to be indicated by a subscript). For example: $E_{cell} =$

$$E_c^{0'} - \frac{RT}{nF} \sum_i \nu_i \ln c_i.$$

⁷¹ This expression for the formal potential ($E_c^{0'}$ or E_f^0) is not suitable

for the one step electro-sorption mechanism.

Similarly, the goal here is to find an expression of the applied potential E , in terms of $c_{A,bulk}$, Γ_B and a bespoke definition of formal potential E_f^0 . When the system is in equilibrium, the adsorption flux of A at the electrode interface equals zero

$$0 = k'_{red} c_{A,0} (\Gamma_{max} - \Gamma_B) \exp(-g^\ddagger \theta_B) - k'_{ox} \Gamma_B \exp((g - g^\ddagger) \theta_B) \quad (Eq. 7.12)$$

and the interfacial concentration $c_{A,0}$ equals to the bulk concentration $c_{A,bulk}$, so substituting Equations 7.10 and 7.11 into Equation 7.12 and rearranging gives

$$k''_{red} e^{-\frac{\alpha F}{RT}E} c_{A,bulk} (\Gamma_{max} - \Gamma_B) \exp(-g^\ddagger \theta_B) = k''_{ox} e^{\frac{(1-\alpha)F}{RT}E} \Gamma_B \exp((g - g^\ddagger) \theta_B) \quad (Eq. 7.13)$$

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Rearrangement gives the applied potential E

$$E = \frac{RT}{F} \left(\ln \left(\frac{k''_{red} c^0}{k''_{ox}} \right) + \ln \left(\frac{c_{A,bulk}}{c^0} \right) + \ln \left(\frac{(\Gamma_{max} - \Gamma_B)}{\Gamma_B} \right) - g\theta_B \right) \quad (Eq. 7.14)$$

Equation 7.14 can be expressed in terms of the concentration of A and surface coverage of B yielding an expression for the formal potential E_f^0

$$E = E_f^0 + \frac{RT}{F} \ln \left(\frac{c_{A,bulk}}{c^0} \right) + \frac{RT}{F} \ln \left(\frac{(\Gamma_{max} - \Gamma_B)}{\Gamma_B} \right), \text{ where } E_f^0 = \frac{RT}{F} \left(\ln \left(\frac{k''_{red} c^0}{k''_{ox}} \right) - g/2 \right) \quad (Eq. 7.15)$$

Note that because k''_{red} ($\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$) and k''_{ox} (s^{-1}) have different units, the standard (unity) concentration c^0 (mol m^{-3}) is introduced to ensure unitless quantities of which to take logarithms. It becomes apparent that the standard formal potential E_f^0 , for a single-step electrodeposition reaction mechanism, is most suitably defined as the potential at which the surface coverage Γ_B at equilibrium is equal to half the maximum coverage in the presence of a standard concentration of the reactant. Note that E_f^0 is mathematically ill-defined if Γ_B defined at equilibrium equals either a monolayer coverage, Γ_{max} , or zero.

7.2.4 Standard Electro-Sorption Rate Constant k'_0

Having defined a bespoke formal potential E_f^0 , it is more insightful to next express the electro-sorption rate constants k'_{red} and k'_{ox} in terms of an applied potential E relative to the E_f^0 . First, the formal potential E_f^0 (Equation 7.15) is introduced to Equations 7.10 and 7.11

$$k'_{red} = k''_{red} e^{\frac{-\alpha F}{RT} E_f^0} e^{\frac{-\alpha F}{RT} (E - E_f^0)} \quad (Eq. 7.16)$$

$$k'_{ox} = k''_{ox} e^{\frac{(1-\alpha) F}{RT} E_f^0} e^{\frac{(1-\alpha) F}{RT} (E - E_f^0)} \quad (Eq. 7.17)$$

By dividing Equation 7.16 by 7.17, the terms in red can be simplified by finding common factors.

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$$\frac{k'_{red}}{k'_{ox}} = \frac{k''_{red}}{k''_{ox}} e^{\frac{-F}{RT} E_f^0} e^{\frac{-F}{RT} (E - E_f^0)} \quad (Eq. 7.18)$$

To simplify the notations, the dimensionless potential $\theta = \left(\frac{F}{RT}\right) (E - E_f^0)$ is substituted into the above equation. Note the subtle but key difference between the uppercase theta (θ) for dimensionless potential and lowercase for fractional surface coverage (θ_B) used elsewhere in the simulation.

$$\frac{k'_{red}}{k'_{ox}} = \frac{k''_{red}}{k''_{ox}} e^{\frac{-F}{RT} E_f^0} e^{-\theta} \quad (Eq. 7.19)$$

Next, the newly defined standard formal potential E_f^0 (Equation 7.15) is substituted into Equation 7.19

$$\frac{k'_{red}}{k'_{ox}} = \frac{k''_{red}}{k''_{ox}} e^{\frac{-FRT}{RT F} \left(\ln \left(\frac{k''_{red} c^0}{k''_{ox}} \right) - g/2 \right)} e^{-\theta} \quad (Eq. 7.20)$$

which simplifies to give

$$\frac{k'_{red}}{k'_{ox}} = \frac{k''_{red}}{k''_{ox}} \frac{k''_{ox}}{k''_{red} c^0} e^{g/2} e^{-\theta} \quad (Eq. 7.21)$$

$$\frac{k'_{red}}{k'_{ox}} = \frac{1}{c^0} e^{g/2} e^{-\theta} \quad (Eq. 7.22)$$

From 7.22 we can deduce that

$$k'_{red} = \text{constant} * e^{-\alpha\theta} \quad (Eq. 7.23)$$

$$k'_{ox} = \text{constant} * c^0 e^{-g/2} e^{(1-\alpha)\theta} \quad (Eq. 7.24)$$

where the mutual constant is termed the standard electro-sorption rate constant k'_0 ($\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$). The expression of electro-sorption rate constants become

$$k'_{red} = k'_0 e^{-\alpha\theta} \quad (Eq. 7.25)$$

$$k'_{ox} = k'_0 c^0 e^{-g/2} e^{(1-\alpha)\theta} \quad (Eq. 7.26)$$

7.2.5 Mathematical Model

Considering the above, the next step is to develop a mathematical model for the electro-sorption reaction shown in Equation 7.1 occurring at a macroelectrode. In the absence of natural convection and with sufficient inert supporting electrolyte, the mass transport of species A(aq) diffusing from semi-infinite solution to a macro-electrode is described by Fick's second law of diffusion in one-dimension

$$\text{all } x, \quad \frac{\partial c_A}{\partial t} = D_A \frac{\partial^2 c_A}{\partial x^2} \quad (\text{Eq. 7.27})$$

where x is the distance from the electrode (m). At the electrode interface, $x = 0$, the rate of the heterogeneous reaction is given by Equation 7.9

$$x = 0, \quad D_A \left(\frac{\partial c_A}{\partial x} \right)_{x=0} = k'_{red} c_{A,0} (\Gamma_{max} - \Gamma_B) \exp(-g^\ddagger \theta_B) - k'_{ox} \Gamma_B \exp((g - g^\ddagger) \theta_B) \quad (\text{Eq. 7.28})$$

where the electro-sorption rate constants $k'_{red/ox}$ were suitably defined (Section 7.2.4) in terms of an applied potential E relative to the standard formal potential E_f^0 , and a standard electro-sorption rate constant k'_0 ($\text{m}^3 \text{mol}^{-1} \text{s}^{-1}$).

For conservation of mass, the rate of change in surface-bound species B is equal to the rate of depletion of A the interface

$$\text{flux } j = -D_A \left(\frac{\partial c_A}{\partial x} \right)_{x=0} = -\frac{\partial \Gamma_B}{\partial t} \quad (\text{Eq. 7.29})$$

In a cyclic voltammetry simulation, initially, the concentration of species A is uniform throughout the solution with a zero coverage of B present

$$t = 0, \quad 0 \leq x \leq x_{max} \quad \begin{cases} c_{A,x} = 1 \\ \Gamma_B = 0 \end{cases} \quad (\text{Eq. 7.30})$$

The potential applied to the electrode E varies linearly with time from a starting potential $E_{initial}$

$$E = E_{initial} - vt \quad (\text{Eq. 7.31})$$

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v is the scan rate (V s^{-1}). At time $t = t_{\text{switch}}$, the potential reaches E_{switch} and the potential sweep changes direction

$$E = E_{\text{switch}} + v(t - t_{\text{switch}}) \quad (\text{Eq. 7.32})$$

The current obtained during the voltammetric sweep is directly related to the flux j at the electrode

$$I = FAj \quad (\text{Eq. 7.33})$$

where I is current (A) and A is the geometric area of the electrode (m^2).

7.2.6 Dimensionless Parameters

The definitions of the dimensionless parameters employed are given in Table 7.1 and are used to report the simulation results. The advantages in using dimensionless parameters as opposed to dimensional parameters, as discussed in Chapter 5, are that; first, the number of independent parameters is reduced to a minimum and consequently, second, the number of simulations required to describe a wide range of experimental conditions is reduced.

Table 7.1. Definition of dimensionless parameters; where r_e is the radius of the disc electrode (m), D_A is diffusion coefficient of species A (m^2s^{-1}) and Γ_{max} is the maximum surface coverage (mol m^{-2}).

Dimensionless parameters		Normalisation
T	Time	$D_A t / r_e^2$
X	spatial coordinates	x / r_e
C_J	concentration of species J	$c_J / c_{A,\text{bulk}}$
θ_B	fractional surface coverage of species B	$\Gamma_B / \Gamma_{\text{max}}$
d_J	diffusion coefficient of species J	D_J / D_A
σ	scan rate	$(r_e^2 / D_A)(F / RT)v$

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B	saturation parameter	$\frac{r_e C_{A,bulk}}{\Gamma_{max}}$
θ	potential	$\left(\frac{F}{RT}\right)(E - E_f^0)$
K'_0	The standard electro-sorption rate constant	$k'_0 \Gamma_{max} r_e / D_A$
K'_{red}	Electro-adsorption rate constant	$k'_{red} \Gamma_{max} r_e / D_A$
K'_{ox}	Electro-desorption rate constant	$k'_{ox} \Gamma_{max} r_e / D_A C_{A,bulk}$
J	flux	$\frac{I}{\pi r_e F D_A C_{A,bulk}}$

The dimensionless diffusion equation becomes

$$0 < X < X_{max} \text{ and } 0 < T < T_{max} \quad \left\{ \left(\frac{\partial C_A}{\partial T} \right)_X = d_A \frac{\partial^2 C_A}{\partial X^2} \right. \quad (Eq. 7.34)$$

The boundary conditions of the model in the dimensionless form:

$$\begin{cases} 0 < T < T_{max} \\ X = 0 \end{cases} \left\{ \begin{aligned} d_A \left(\frac{\partial C_A}{\partial X} \right)_{X=0} &= K'_{red} C_{A,0} (1 - \theta_A) e^{-g^\ddagger \theta_B} - K'_{ox} \theta_B e^{(g-g^\ddagger) \theta_B} \\ Flux J &= -d_A \left(\frac{\partial C_A}{\partial X} \right)_{X=0} = -\frac{1}{B} \frac{\partial \theta_B}{\partial T} \end{aligned} \right. \quad (Eq. 7.35)$$

Here, the dimensionless electro-sorption rate constants $K'_{red/ox}$ are equal to

$$K'_{red} = K'_0 e^{-\alpha \theta} \text{ and } K'_{ox} = K'_0 C^0 e^{-g/2} e^{(1-\alpha) \theta} \quad (Eq. 7.36)$$

where θ is the dimensionless applied potential relative to the formal potential E_f^0

$$\theta = \frac{F}{RT} (E - E_f^0) \quad (Eq. 7.37)$$

At the start of the cyclic voltammetry simulation

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$$T = 0 \quad \begin{cases} C_A, X = 1, & \text{for } 0 \leq X \leq X_{max} \\ \theta_B = 0 \end{cases} \quad (\text{Eq. 7.38})$$

During the simulation, the dimensionless applied potential θ varies linearly with dimensionless time T and dimensionless scan rate σ

$$\theta = \theta_{initial} - \sigma T \quad (\text{Eq. 7.39})$$

When $T = T_{switch}$, the sweep direction is reversed

$$\theta = \theta_{switch} + \sigma(T - T_{switch}) \quad (\text{Eq. 7.40})$$

The dimensionless flux J at the electrode surface is

$$J = -d_A \left(\frac{\partial C_A}{\partial X} \right)_{X=0} \quad (\text{Eq. 7.41})$$

The dimensionless flux J can convert back to dimensional current (A) for a macro-disc electrode via the equation

$$I = \pi r_e F D_A C_{A,bulk} J \quad (\text{Eq. 7.42})$$

7.2.7 Numerical Simulation and Convergence

The diffusion equation for the one-dimensional simulation was discretised using the Backward Implicit Method^{72, 73} with a uniform temporal grid and a spatial grid that expands exponentially⁷⁴ from the electrode surface X_0 to X_{max}

$$X_i = \begin{cases} X_0 = 0 \\ X_i = X_{i-1} + h * \exp(i\omega), & \text{for } X_i < X_{max} \\ X_i = X_{max} & , \text{for } X_i \geq X_{max} \end{cases} \quad (\text{Eq. 7.43})$$

$$X_{max} = 6\sqrt{T_{max}} \quad (\text{Eq. 7.44})$$

where h is the initial grid spacing, ω is the expansion factor and X_{max} is the extent of the dimensionless distance defined well beyond the Nernst diffusion layer⁷⁵ for the duration of the simulation T_{max} .^{74, 76} The matrix containing the sets of discretised diffusion equations, including the non-linear term for the heterogeneous reaction, were solved via

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the Newton-Raphson's root-finding method using the extended Thomas algorithm.⁷⁴ The values of the incremental spatial, temporal point, expansion factor and Newton-Raphson's tolerance level (ϵ) were set to a small value to ensure numerical convergence and mass conservation for each simulation.⁷⁷ The simulations were written in C++ and ran on a dual Intel (R) Core (TM) E5-2640 v4 CPU 2.40 GHz PC with 16.00 GB of RAM, with a typical run time of approximately one minute. All simulation results were thoroughly checked and benchmarked with two limiting cases as described below, with more data shown in the Appendix B.

Limiting Case One

First, the forward electro-sorption step together with the mass transport of species A was checked; in the limiting case of a small K'_0 leading to an irreversible deposition *and* a sufficiently large surface coverage, such that less than 1% of the sites are occupied, the resulting peak flux matches with that predicted by the irreversible Randles–Ševčík equation^{78, 79} with an excellent agreement (Appendix B)

$$J_{peak, \text{ limiting Case One}} = -0.496\sqrt{\alpha\sigma} \quad (\text{Eq. 7.45})$$

where $J_{peak, \text{ limiting Case One}}$ is the dimensionless peak flux. Furthermore, the dimensionless peak potential $\theta_{peak, \text{ irreversible}}$ matches that predicted for irreversible electrode kinetics (Appendix B).⁷⁴

$$\theta_{peak, \text{ limiting Case One}} = \frac{1}{\alpha} \ln \left(\frac{K'_0}{\sqrt{\alpha\sigma}} - 0.78 \right) \quad (\text{Eq. 7.46})$$

Limiting Case Two

Similar to Case One, the electro-desorption of the surface-bound B can be benchmarked in the limiting case of a small K'_0 . Here, for $T = 0$, the initial coverage θ_B is set to unity with the voltammetric sweep in the anodic direction to drive the oxidation of $B(ads) \rightarrow A(aq)$; an analytical expression for flux J can be derived when the surface interactions

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are ideal, $g = g^\ddagger = 0$, giving an expression of flux J as a function of dimensionless applied potential θ (see Appendix B for a step-by-step derivation)

$$J_{\text{limiting Case Two}} = K'_0 e^{\frac{-K'_0 B}{(1-\alpha)\sigma}} e^{(1-\alpha)\theta + (1-\alpha)\theta} \quad (\text{Eq. 7.47})$$

Furthermore, the dimensionless peak potential ($\theta_{\text{peak, limiting case 2}}$) and dimensionless peak flux ($J_{\text{peak, limiting case 2}}$) can be obtained when the derivative $J_{\text{limiting case 2}}$, with respect to θ , equals zero

$$\theta_{\text{peak, limiting Case Two}} = \frac{1}{1-\alpha} \ln \left(\frac{(1-\alpha)\sigma}{B} \frac{1}{K'_0} \right) \quad (\text{Eq. 7.48})$$

$$J_{\text{peak, limiting Case Two}} = (1-\alpha)\sigma B^{-1} e^{-1} \quad (\text{Eq. 7.49})$$

7.3 Results and Discussion

The mathematical model discussed above describes the one-step electrosorption reaction (Equation 7.1) where a solution phase species $A(aq)$ transfers an electron at the electrode interface to form a surface-bound product with maximum coverage of a monolayer. Specifically, Butler-Volmer kinetics are coupled with the Frumkin adsorption isotherm providing a rate expression for the heterogeneous reaction allowing non-ideal surface interactions to be studied in terms of the Frumkin adsorbate-adsorbate interaction parameter g .

In the following results and discussion, we provide new physical insights on how the non-ideal surface interactions coupled with mass transport affects the current-voltage transient in a typical voltammetry experiment, in which the dynamically applied potential changes with time, notably the classical triangular potential waveform in cyclic voltammetry which will inevitably lead to mass transport induced dis-equilibrium in the vicinity of the electrode. First, however, we consider the Frumkin adsorption isotherm where *both* mass

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transport and adsorption-desorption are in equilibrium to understand the possible non-ideal surface interactions more fully and focus on the emergence of phase transition behaviour in the voltammetry for strongly attractive surfaces interactions.

7.3.1 Phase Transitions Simulated for Equilibrium; No Mass Transport Limitations

In this section, the effect of surface interaction parameter g for Frumkin adsorption isotherm is discussed in the context of the electro-sorption reaction under mass transport and surface reaction equilibrium. First, a common ground between the adsorption isotherm and electro-sorption isotherm has to be established for direct comparison. Hereafter in the Chapter, the notation of the fractional surface coverage for pure adsorption-desorption processes will be unified with that used in the electro-sorption reaction (i.e. $\theta = \theta_B$) to avoid possible confusion.

The common ground that both the adsorption isotherm and the electro-sorption reaction share is a thermodynamic equilibrium position controlled by the rate of the corresponding forward and backward reactions. Here, a dimensionless equilibrium constant K is introduced, allowing a direct comparison between the two equilibria. For pure adsorption-desorption, the dimensionless equilibrium constant K is equal to $\frac{k_{ads}}{k_{des}} c_{A,bulk}$. A similar expression for the electro-sorption reaction can be obtained when flux, either in the dimensional form (Equation 7.28) or the dimensionless equivalent Equation 7.35, is equal to zero

$$K = \frac{K'_{red}}{K'_{ox}} = \frac{k'_{red}}{k'_{ox}} c_{A,bulk} \quad (Eq. 7.50)$$

This leads to the expression relating the dimensionless equilibrium constant K to the fractional coverage θ_B

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$$KC_{A,0} = \frac{\theta_B}{1-\theta_B} \exp(g\theta_B) \quad (\text{Eq. 7.51})$$

Note that, the dimensionless interfacial concentration $C_{A,0}$ is equal to $c_{A,0}/c_{A,bulk}$; in the case of the system at equilibrium, $c_{A,0}$ equals $c_{A,bulk}$ and thus $C_{A,0}$ is unity. We leave the notation $C_{A,0}$ as is in this section.

Figure 7.1 shows a plot of $\theta_{B, \text{equilibrium}}$ against $KC_{A,0}$, for different Frumkin interaction parameter g . Solid lines show the prediction from Frumkin adsorption isotherm and circles are results from the electro-sorption simulation when the system is at equilibrium. For all cases of g , whether attractive, ideal or repulsive adsorbate-adsorbate interactions, an increase in $KC_{A,0}$ leads to an increase in the fractional coverage of θ_B at equilibrium. Excellent agreement is seen between the simulation results and the Frumkin adsorption isotherm for all values of $KC_{A,0}$ over the full range of g studied. As g becomes increasingly negative, the surface interaction becomes increasingly attractive and a lower $KC_{A,0}$ is required to reach half fractional coverage as indicated by the dashed line.

The physical meaning of $KC_{A,0}$ varying along the x-axis can be interpreted with experimental conditions; under system equilibrium, the dimensionless concentration at the electrode interface $C_{A,0}$ is trivially unity thus it is K that changes along the x-axis. From the definition of K for adsorption isotherms, this is a change in the *dimensional* bulk concentration ($c_{A,bulk}$) since the ratio of k_{ads}/k_{des} is a constant “given by the universe”. For the electro-sorption reaction, however, K can be changed either by $c_{A,bulk}$ and/or the applied potential (Equations 7.25 and 7.26)

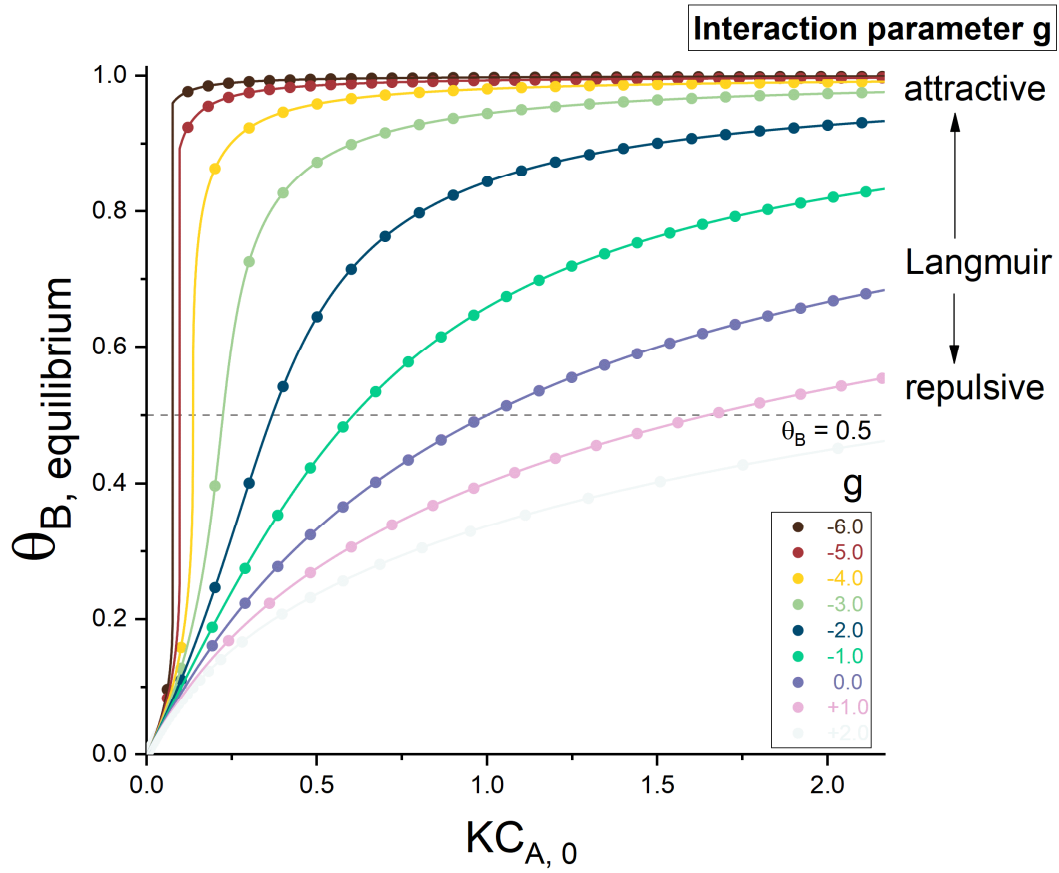


Figure 7.1. Plot of $\theta_{B, equilibrium}$ vs $KC_{A,0}$ from the Frumkin adsorption isotherm for a range of interaction parameter g (solid lines). Circles: simulation results obtained by setting C_A over all space to unity until equilibrium are established with no more than 10^{-7} % change in the fractional coverage from the last iteration.

Figure 7.2 shows the equivalent plot of Figure 7.1 but with normalisation in the x-axis to the value of $KC_{A,0}$ leading to half fractional coverage at equilibrium ($KC_{A,0}/K_{\theta_B=0.5}$).

Substitution of $C_{A,0} = C_{A,bulk}$ and $\theta_B = 0.5$ into Equation 7.51 gives

$$K_{\theta_B=0.5}C_{A,bulk} = \exp\left(\frac{g}{2}\right) \quad (Eq. 7.52)$$

This normalisation standardises the plots of all g in Figure 7.2 resulting in an ‘isobestic point’ like behaviour when $KC_{A,0}/K_{\theta_B=0.5}$ equals unity. It now becomes apparent that, as the interactions between the surface-bound species become increasingly attractive (negative g), the θ_B vs $KC_{A,0}/K_{\theta_B=0.5}$ transient becomes more and more sigmoidal. When g approaches -4.0 (yellow line), a sudden and abrupt change in θ_B can be seen near unity of $KC_{A,0}/K_{\theta_B=0.5}$ indicating a “phase transition like” behaviour. When g is

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more negative than -4.0 , a counter-intuitive ‘S-shape’ transient about $\theta_B = 0.5$ and $KC_{A,0}/K_{\theta_B=0.5} = 1$ can be seen. From this one infers that there is a sudden jump from a low to high coverage as shown by the dashed line in Figure 7.2 a) since physically an increasing $\frac{KC_{A,0}}{K_{\theta_B=0.5}}$ cannot ‘fall back’ on itself. Therefore, the region where the curve changes direction with respect to the x-axis can be thus viewed as “forbidden”. The above phenomenon is next simulated using the developed simulation model for the values of g discussed. The results are overlaid in Figure 7.2.

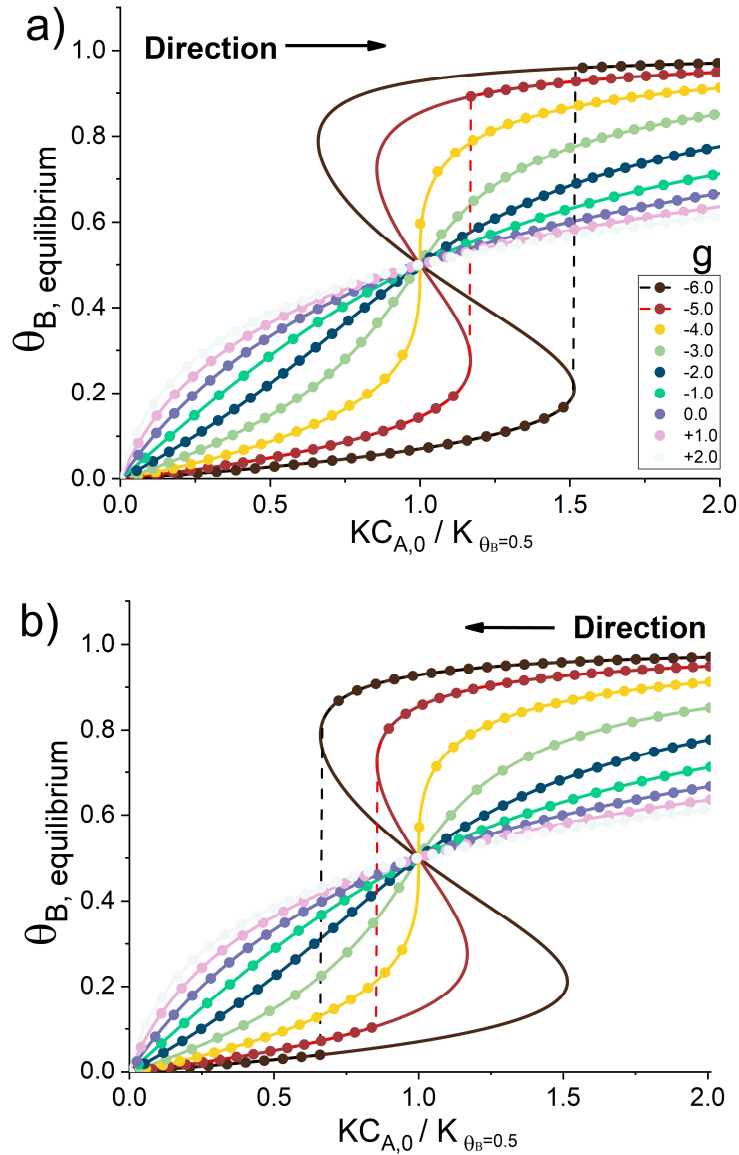


Figure 7.2. Plot of $\theta_{B, equilibrium}$ vs $KC_{A,0}/K_{\theta_B=0.5}$ for different values of interaction parameter g . The solid line shows the analytical Frumkin adsorption isotherm. The overlaid circles are the simulation results

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with either (a) an incremental increase in $KC_{A,0}/K_{\theta_B=0.5}$ from zero or (b) incremental decrease in $KC_{A,0}/K_{\theta_B=0.5}$ from 2.0. The dashed lines infer the sudden jump in coverage of B.

To mimic the equilibration between the solution and the electrode layer in the simulation, the concentration of species A over the entire simulation space was set initially to $C_{A,bulk}$ and the simulation allowed to iterate but with the solution concentration reset to $C_{A,bulk}$ after each temporal iteration, until the fractional coverage θ_B reaches equilibrium with the bulk solution. The equilibrium was considered established when the fractional change in the coverage of θ_B was no more than 10^{-7} % from the previous temporal iteration. Figure 7.2 shows θ_B as a function of $KC_{A,0}/K_{\theta_B=0.5}$ for two cases; first when $KC_{A,0}/K_{\theta_B=0.5}$ is incrementally increased from zero and second when it is decreased from a large value corresponding to a high, near unity, coverage of B. These data were shown as circles for different g . In all cases of g , and both direction of changes in $C_{A,bulk}$, the simulation results all overlaid on the transient as predicted by the Frumkin adsorption isotherm (solid lines). For the non-phase transition g studied ($-4.0 < g \leq +2.0$), the results were independent to the direction of change in $C_{A,bulk}$. When g equal to -4.0 , a vertical gradient between $\theta_{B,equilibrium}$ from 0.4 to 0.6 can be seen when $KC_{A,0}/K_{\theta_B=0.5}$ approaches unity. When g is more negative than -4.0 , a point of discontinuity from the sigmoidal transient is seen with $\theta_{B,equilibrium}$ changing abruptly from 0.2 to 0.9 for an increase in $KC_{A,0}/K_{\theta_B=0.5}$ and from 0.9 to 0.2 for a decreasing in $KC_{A,0}/K_{\theta_B=0.5}$ as discussed above; note that the simulated data do not enter the ‘forbidden’ part of the sigmoidal curve where the horizontal direction of the analytical curve is opposite to the direction of change in $KC_{A,0}/K_{\theta_B=0.5}$. These abrupt changes in fractional coverage signal a phase transition, and it only occurs with values of $g \leq -4.0$.

Having understood the effects of non-ideal surface interaction under the conditions of both surface kinetics and mass transport equilibrium. The focus now turns to

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voltammetric studies where the dynamic change in applied potential with time may not necessarily be kinetically reversible nor in mass transport equilibrium near the vicinity of the electrode.

7.3.2 Cyclic Voltammetry: Non-ideality Leading to Phase Transitions

This section aims to provide new physicochemical insights on how the non-ideal adsorbate-adsorbate interaction, g , affects the cyclic voltammograms of the electro-sorption reaction under planar diffusion conditions. First, the influence of g on voltammograms is studied for the case of reversible electro-sorption kinetics (K'_0). Second, for each value of g , the effects of the K'_0 (extent of reversibility), are studied. Then the effect of $g^\ddagger$, the activated complex (transition state) – adsorbate interaction parameter, is briefly investigated for different values of g . Finally, the focus turns to investigate the effects of mass transport on the cyclic voltammograms and, in particular, for the case where a critical value of g leads to a phase transition.

Simulated voltammograms as a function of g and corresponding to fast and reversible electro-sorption kinetics ($K'_0 = 100$) are shown in Figure 7.3. Here, the term fast (or slow) kinetics is relative to the mass transport under ideal surface interactions $g = 0$. Other simulation parameters are: $B = 100, \sigma = 100, \alpha = 0.5, g^\ddagger = 0$. For all cases of g , a cathodic peak is seen during the forward sweep with the dimensionless flux J subsequently returning to zero corresponding to full coverage of B which precludes any full ‘diffusional tail’ being seen; similarly, anodic stripping peaks are seen on the reverse sweeps. During the reverse stripping sweep, the surface-bound B is driven to form $A(aq)$ leading to an anodic stripping peak after which the flux returns to zero when $B(ads)$ becomes fully depleted. In the ideal case where the adsorbate-adsorbate surface

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interactions (g) equals to zero, the voltammogram is symmetric resembling a surface-bound redox process, $A(ads) + e^- \rightleftharpoons B(ads)$ under fast electrode kinetics due to the excess of $A(aq)$ at the electrode surface in comparison with the number of sites available. If the interactions on the surface become repulsive ($g > 0$), the voltammogram appears ‘flattened’ compare to the ideal case because a higher over-potential is required to drive the forward deposition reaction as the repulsive interaction on the surface scales with coverage. On the other hand, the voltammetric wave-shape becomes sharper and narrower for attractive surface interactions ($g < 0$). This is due to the attractive surface interaction, scaling with surface coverage, providing an additional driving force for the deposition. Furthermore, as g approaches to the critical phase transition values of -4.0 or beyond, the peak current surges to a large value once the reaction has begun, as shown by the ‘zoom-out’ plot in the inlay of Figure 7.3. Furthermore, the peak-to-peak separation increases when g is beyond the critical value of -4.0 indicating an increase in the degree of irreversibility at $K'_0 = 100$, of which more is discussed below.

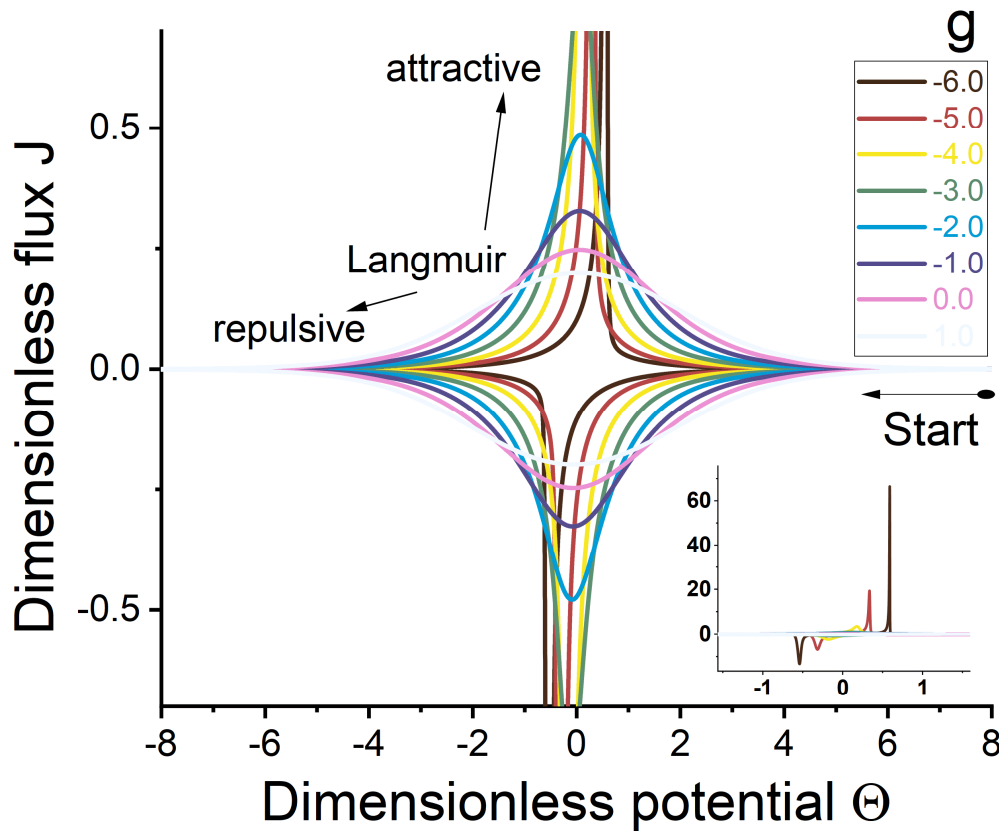


Figure 7.3. Simulated voltammograms as a function of surface interaction parameter g under reversible electrode kinetics. The values of g are shown in the figure. Other simulation parameters: $K'_0 = 100$, $B = 100$, $\sigma = 100$, $\alpha = 0.5$ and $g^\ddagger = 0$.

Figure 7.4 shows a series of simulated voltammograms varying dimensionless standard electro-sorption rate constant K'_0 , from 10^6 to 10^{-3} , for a range of g values. The other simulation parameters are the same as in Figure 7.3 ($B = 100$, $\sigma = 100$, $\alpha = 0.5$, $g^\ddagger = 0$). The general feature seen across all values of g is an increase in peak-to-peak separation $\Delta\theta_{pp}$ ($\theta_{anodic\ peak} - \theta_{cathodic\ peak}$) as K'_0 decreases. Changes in the cathodic and anodic peak fluxes are also seen but are different for attractive and repulsive surface interactions. In the case when the surface interactions are ideal, g equals zero, both the anodic and cathodic peak flux decrease asymptotically to a constant value as K'_0 decreases to a fully irreversible limit at 10^{-3} . For repulsive surface interaction, g is equal to $+2.0$, the cathodic peak flux increases as K'_0 approaches 10^{-3} whilst the anodic peak flux decreases. On the other hand, for attractive surface interactions ($g = -2.0$) the

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magnitude of the cathodic peak flux is more than halved as the electrode kinetics turns fully irreversible; this phenomenon is amplified as g decreases to -4.0 and -5.0 .

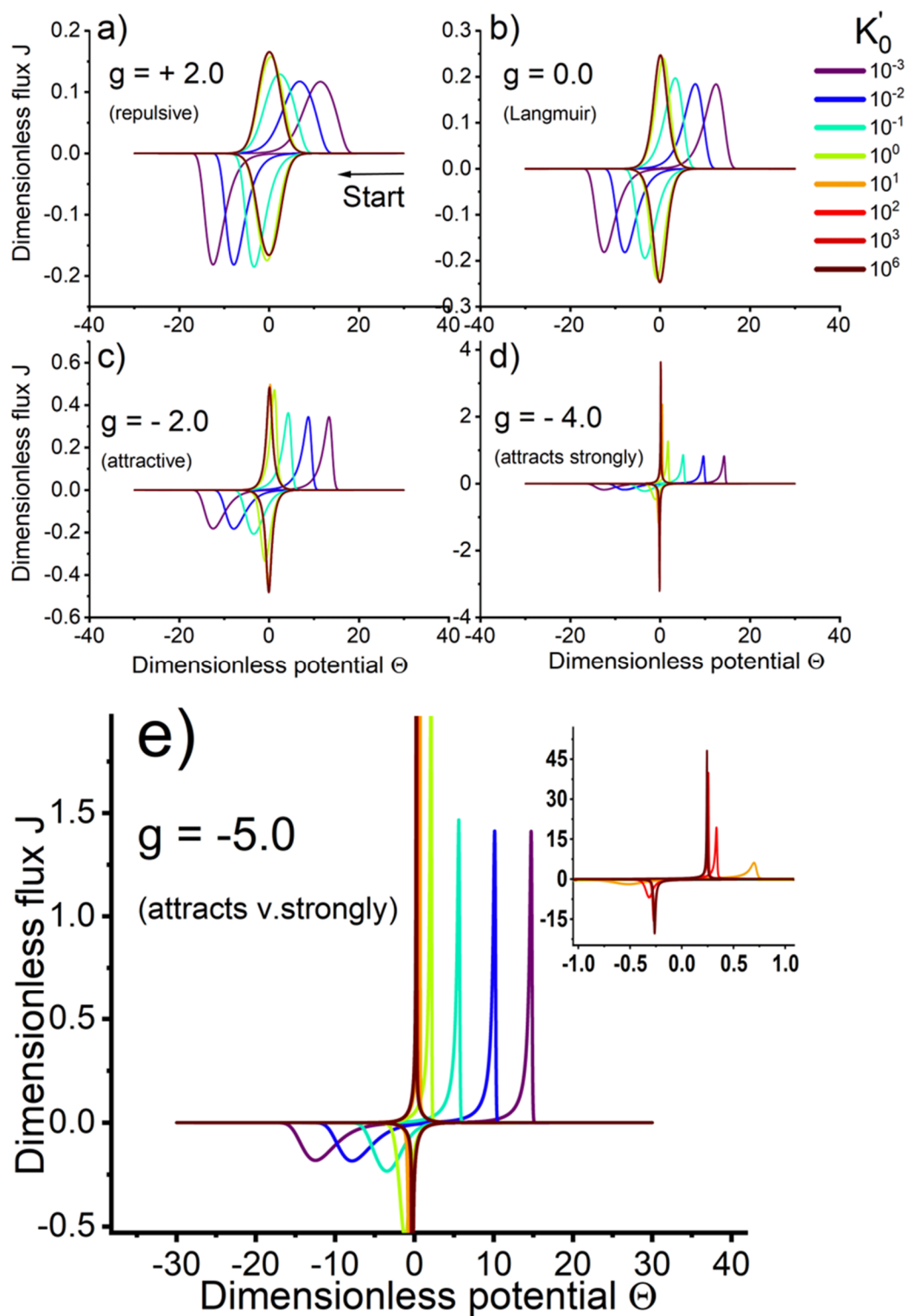


Figure 7.4. Simulated voltammograms as a function K'_0 ranging from 10^{-3} to 10^6 for different values of g . The values of g and K'_0 can be found in the figure. Other simulation parameters: $B = 100$, $\sigma = 100$, $\alpha = 0.5$ and $g^\ddagger = 0$.

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An interesting observation can be seen in Figure 7.4, at $g = 0$, notably that full electrode reversibility was achieved at $K'_0 = 10^1$ as higher orders of magnitude of K'_0 result in identical voltammograms. In comparison for $g = -5.0$, the magnitude of peak flux at $K'_0 = 10^1$ is ca one order below that seen at $K'_0 = 10^6$ (inlay of Figure 7.4 d). It is evident that a higher threshold of K'_0 is necessary to reach the limit of full electrode reversibility as g becomes more negative, particularly when g approaches the critical value for a phase transition. This is as expected as the electrode reversibility reflects the interplay between surface kinetics and mass transport in the solution phase,^{80, 81} thus indicating that the changes in the interfacial concentration of species A ‘outrun’ their replenishment by mass transport at negative g . To evidence this and to investigate the possibility of phase transition occurring under voltammetry conditions when $g \leq -4.0$, we next utilise the numerical simulation to provide further insight to the underlying physicochemical processes giving rise to the sharp voltammetric peaks seen in Figure 7.4.

Figure 7.5 shows the fractional surface coverage of B and the corresponding concentration profiles of A for the voltammograms seen in Figure 7.4. Figure 7.5 a) plots the surface coverages of B for different surface interactions (g) simulated for irreversible electrode kinetics ($K'_0 = 10^{-2}$). The case for reversible electrode kinetics ($K'_0 = 10^6$) is shown in Figure 7.5 c). The x-axis is time normalised over the timescale of the simulation. In the case of irreversible electrode kinetics, the surface coverage during the forward sweep ($\frac{T}{T_{max}} < 0.5$) are relatively insensitive to the surface interaction parameter g as over-potential is required to drive the sluggish reaction to overcome the effect of repulsive interaction; in contrast, under reversible electrode kinetics, the surface interaction g has a rather profound impact on the surface coverage of B during the forward sweep. As g becomes increasingly negative, a rapid increase in fractional

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coverage is seen due to the attractive adsorbate-adsorbate interactions. Under reversible electrode kinetics and with g satisfying phase transition (≤ -4.0) the slope of θ_B versus T is vertical as can be seen in the inlays of Figure 7.5 c).

Figure 7.5 b) and d) show the concentration profiles of A simulated for $g = -5.0$ under irreversible and reversible electrode kinetics, respectively. As can be seen, in both cases, the interfacial concentration does not equal to the bulk concentration once the interfacial reaction is driven by the triangular potential waveform; for reversible electrode kinetics, Figure 7.5 d), a sharp drop in the interfacial concentration, $C_{A,0}$, is seen around $\frac{T}{T_{max}} = 0.2$ compared to that seen with irreversible electrode kinetics (Figure 7.5 b). This, together with a vertical gradient of the surface coverage, indicate that reversible electrode kinetics are *essential* in capturing signs of a phase transition on the time scale of a typical voltammetric experiment.

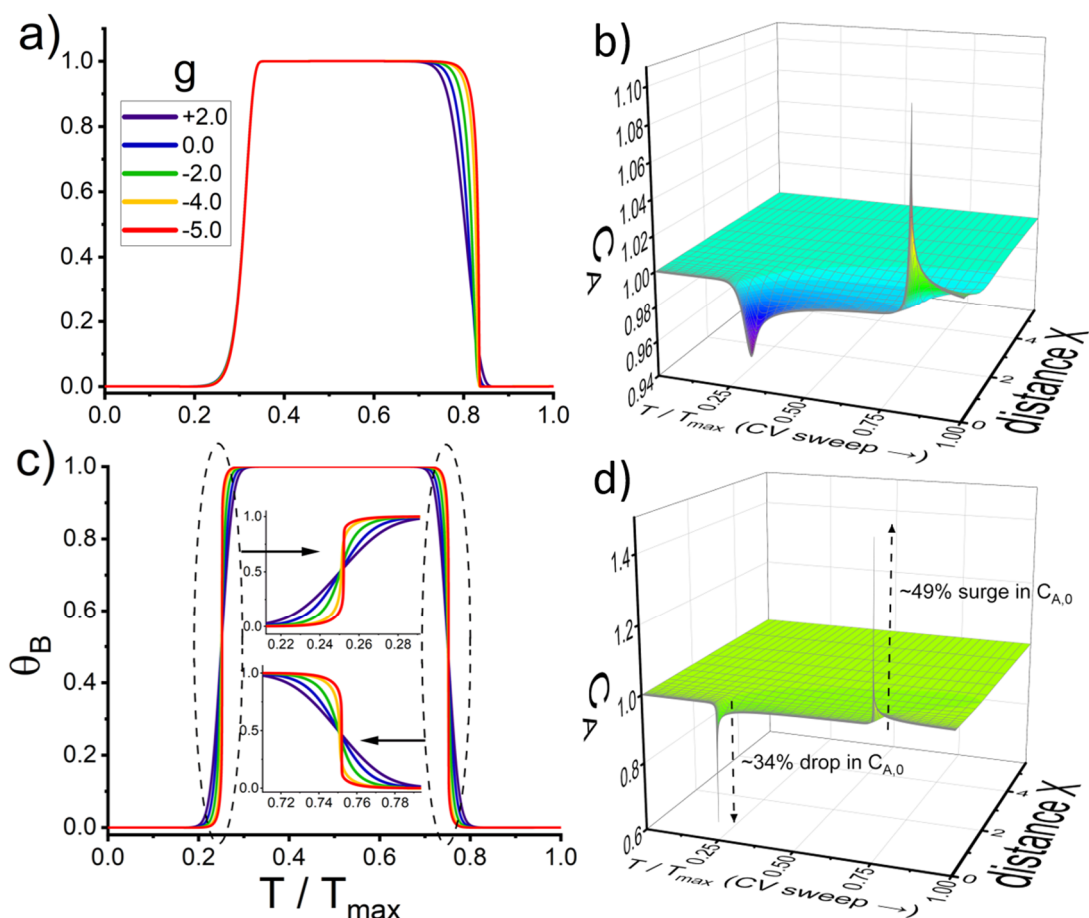


Figure 7.5. A selection of surface coverages and concentration profiles in above simulated cyclic voltammograms, as seen in Figure 7.4, are plotted. Surface coverages as a function of g : a) irreversible electrode kinetics, $K'_0 = 10^{-2}$; c) reversible electrode kinetics, $K'_0 = 10^6$. Concentration profile of $A(aq)$ for $g = -5.0$: b) irreversible electrode kinetics, $K'_0 = 10^{-2}$; d) reversible electrode kinetics; $K'_0 = 10^6$. Other simulation parameters: $B = 100$, $\sigma = 100$, $\alpha = 0.5$ and $g^\ddagger = 0$.

An important question to pose is, how does this abrupt change in θ_B and $C_{A,0}$ seen during the voltammetric timescale relate to the plot of Frumkin adsorption isotherm in Figure 7.2? And, to what extent does un-equilibrated mass transport during the voltammetry affect the phase transition? To shed light on those questions underpinning the physicochemical processes occurring during the voltammetry timescale, we show the same data for the Frumkin adsorption isotherm as in Figure 7.6. The x- and y-axes remain the same as Figure 7.2, θ_B vs $\frac{KC_{A,0}}{K\theta_B + 0.5}$. In the voltammetric experiments, the triangular potential waveform drives the interfacial electro-sorption reaction leading a perturbation of concentration of $A(aq)$ near the vicinity of the electrode, which is evident in the

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concentration profiles shown in Figure 7.5. We have established that Equation 7.51 involving the dimensionless equilibrium constant K are general for both the electro-sorption reaction and Frumkin adsorption isotherm. For Figure 7.6, the electro-sorption equilibrium constant K is potential dependant with the interfacial concentration $C_{A,0}$ and the coverage θ_B known from the numerical simulation. Overlaid in Figure 7.6 are the numerical data from voltammograms seen Figure 7.4, for (a) $K'_0 = 10^{-2}$ corresponding to irreversible and (b) $K'_0 = 10^6$ for reversible electrode kinetics. The circles are data obtained during the forward sweep, and the triangles are data from the reverse sweep of the simulated voltammetry. The direction of travel for the forward sweep is positive on the x-axis ($K \propto e^{-\theta}$, $\theta_{initial} = +30$) whereas that for the reverse sweep is negative on the x-axis ($\theta_{switch} = -30$). For irreversible electrode kinetics, Figure 7.6 a), the reaction at the surface is sluggish and it is unresponsive to the instantaneous changes in potential leading to a ‘disconnection’ from the Frumkin isotherm for all cases of g . In the case where electrode kinetics is fast and reversible, Figure 7.6 b), matches with the Frumkin adsorption isotherm with an excellent agreement for all values of g and both forward and backward sweeps. Interestingly, the cases when the interaction parameter g is beyond the critical value for phase transition, i.e. $g < -4.0$, the surface θ_B transits into the ‘forbidden’ region of the Frumkin adsorption isotherm. The latter is *not* due to $K(\theta)$ since the dimensionless potential θ is varied linearly but thus must result from a local change in concentration of $A(aq)$ on the timescale of voltammetry. The concentration profile of $g = -5.0$ can be seen in Figure 7.5 d), where a drop of approximately 34% of the interfacial concentration compare to bulk solution was observed during the forward sweep. At the same time, a positive and vertical slope of surface coverage against time is seen in Figure 7.4 c), red line. It can be concluded that transition into the ‘forbidden zone’

is a result of the non-equilibrated interfacial concentration under the dynamically changing voltammetric conditions.

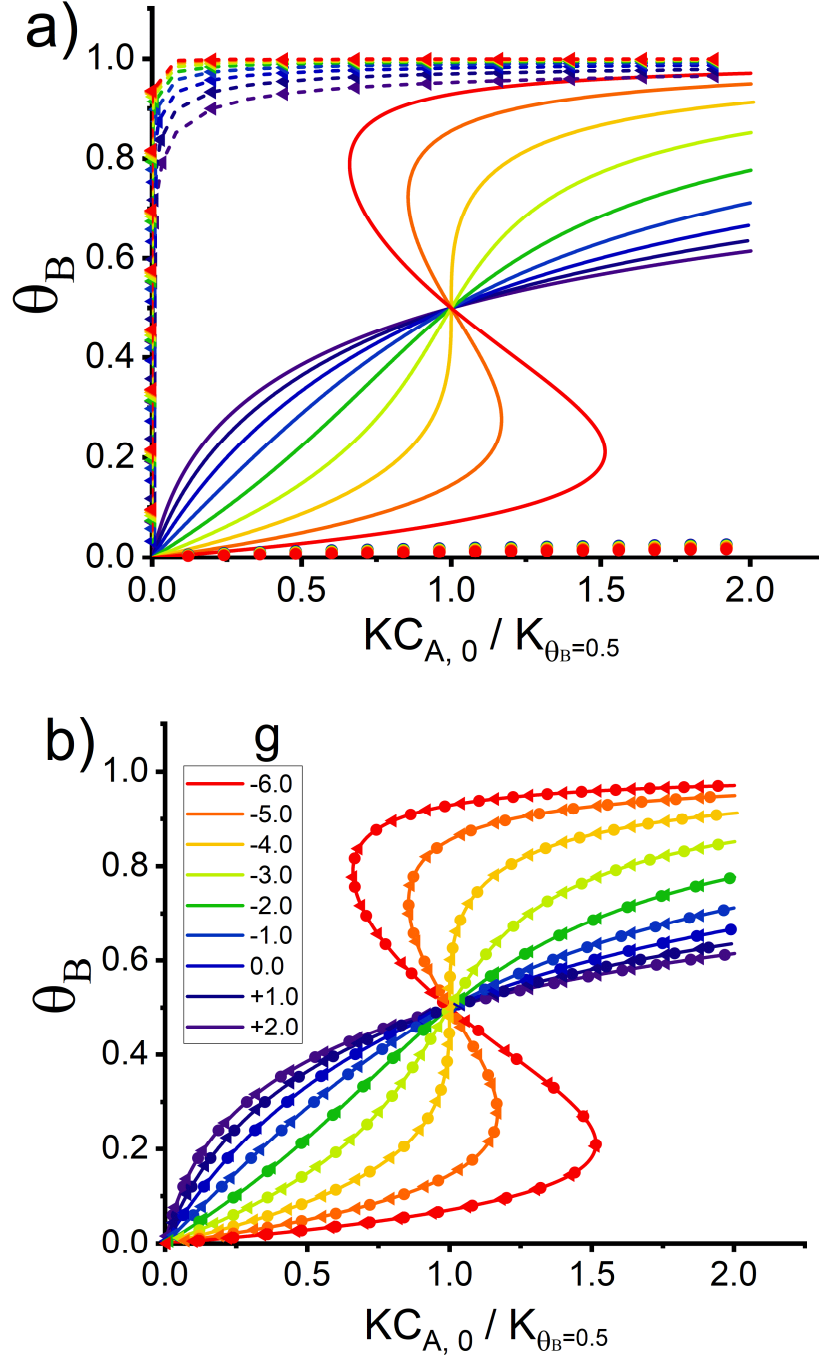


Figure 7.6. A plot of θ_B against $KC_{A,0}/K_{\theta_B=0.5}$ as a function of surface interaction parameters g . The numerical data obtained from the voltammograms in Figure 7.4 are shown; a) irreversible electrode kinetics $K'_0 = 10^{-2}$ and b) reversible electrode kinetics $K'_0 = 10^6$. Specifically, the data from the forward sweep is shown as circles with triangles represent the backward sweep. Solid line shows the analytical prediction for the Frumkin adsorption isotherm plotted in both a) and b). The additional dashed lines in a) are used to enhance the visibility of the data for the backward sweep (triangles). The values of g are shown in the figure. Other simulation parameters: $B = 100$, $\sigma = 100$, $\alpha = 0.5$ and $g^\ddagger = 0$.

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Having understood the behaviour of g and the effects that it has on voltammetry under both reversible and irreversible conditions, attention next turns to investigate the effect of $g^\ddagger$, the transition state-adsorbate interaction parameter, as a function of different values of g .

The value of $g^\ddagger$, neither negative nor positive, has no effect on the voltammograms under reversible electrode kinetics. The simulated voltammograms for $g^\ddagger = 0$ is shown as the solid line in Figure 7.7 for different values of g . Overlaid as dotted lines, in matching colour, is that when $g^\ddagger$ is half the value of g . In all cases, the dotted and solid line overlay perfectly on top of each other and hence $g^\ddagger$ has a negligible effect under reversible electrode kinetics. This is reasonable as the activation energy becomes unimportant when the interfacial reaction is at thermodynamic equilibrium.

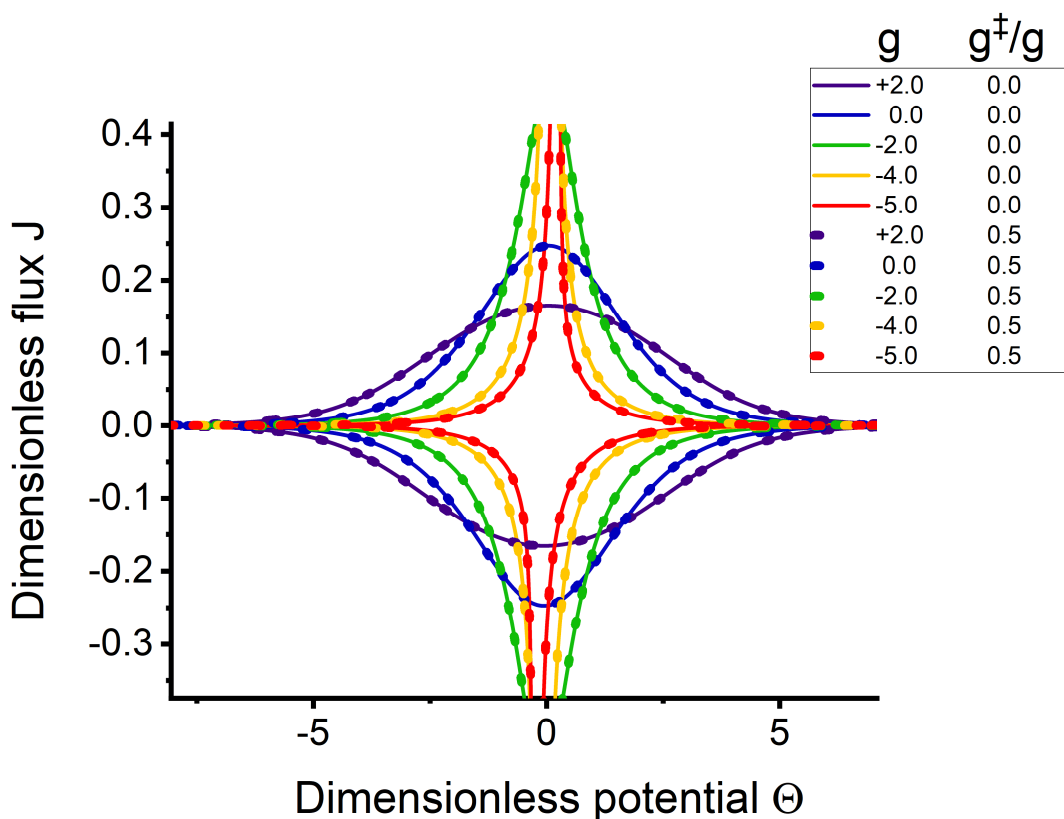


Figure 7.7. Series of voltammograms varying $g^\ddagger$ for different values of g . Other simulation conditions: $K'_0 = 10^6$, $B = 100$, $\sigma = 100$, $\alpha = 0.5$.

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Figure 7.8 shows the series of voltammograms under irreversible electron kinetics ($K'_0 = 10^{-2}$). The realistic values of $g^\ddagger$ may take any value from zero up to the value of g since the transition state likely partially resembles that of the product on the electrode surface. For positive values of g and $g^\ddagger$, Figure 7.8 a), the peak-to-peak separation is increased and this can be interpreted as related to an increase in the activation energy for the overall reaction. For negative values of $g^\ddagger$, Figure 7.8 c)-e), the peak-to-peak separations decrease with an increasingly negative $g^\ddagger$. This is interpreted as a decrease of activation energy of the overall reaction.

In this section the independent parameters controlling the interfacial reaction, namely K'_0 , g and $g^\ddagger$, have been investigated. It can be inferred that fast and reversible electrode kinetics are essential to observe phase transition in the voltammetric timescale when the critical value of g is satisfied (≤ -4.0). The interfacial conditions simulated during the voltammetry induced phase transition reveal intrusions into the ‘forbidden’ part predicted by the Frumkin adsorption isotherm, which are otherwise inaccessible to the prediction on the assumption of mass transport equilibrium. Furthermore, it is to note that the transition state - adsorbate interaction ($g^\ddagger$) does not affect voltammetry involving the behaviour of phase transition as observation of the latter requires reversible electrode kinetics. The next section investigates if, and how, mass transport of the solution phase species A affects voltammetry even if high concentrations of A are used – in particular in the event of phase transition involving a rapid drop in the interfacial concentration is seen.

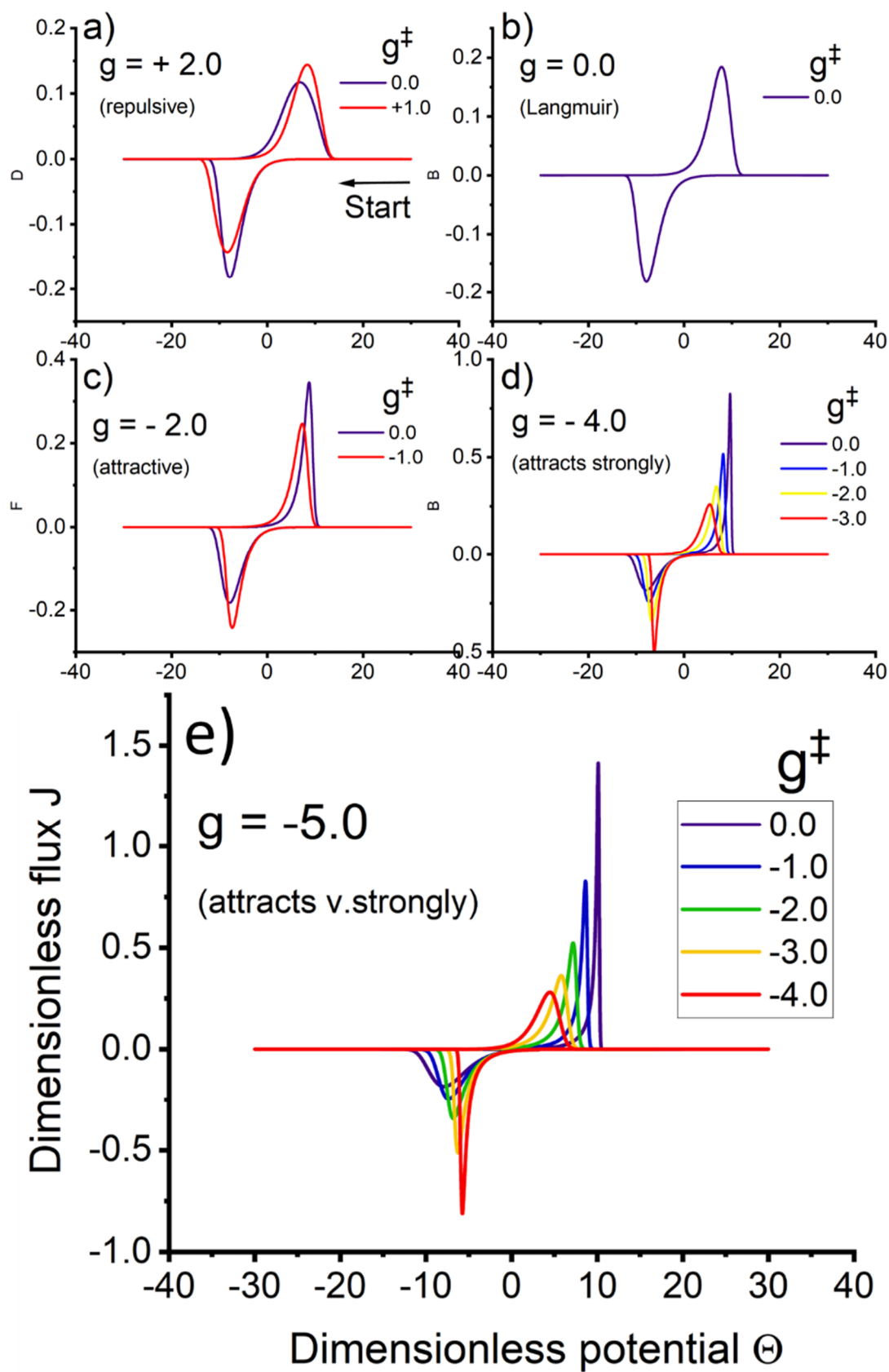


Figure 7.8. Series of voltammograms varying $g^\ddagger$ for different values of g . The values of g and $g^\ddagger$ are shown in the figure. Other simulation conditions: $K'_0 = 0.01$, $B = 100$, $\sigma = 10$ and $\alpha = 0.5$.

7.3.3 Cyclic Voltammetry: Effect of Mass Transport

Hitherto, the underlining physicochemical processes of the electro-sorption reaction with non-ideal surface interactions leading to phase transition were studied at a dimensionless scan rate of $\sigma = 100$ and saturation parameter $B = 100$, where the latter is the ratio of bulk concentration of A to the total coverage (see Table 7.1). These parameters, for a 1mm macro-disc electrode and with a typical diffusion coefficient ($D_A = 1 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) correspond to experimental conditions of $c_{A,bulk} = 1 \text{ mM}$, $\Gamma_{max} = 10^{-5} \text{ mol m}^{-2}$ and $v \approx 3 \text{ mVs}^{-1}$. In literature studies, analytical expressions used to estimate g from the voltammetric peak width typically assume a diffusionless system, i.e. $C_{A,0} = C_{A,bulk}$ at all times, justified by the experimental use of a large concentration of the reactant (0.1 M) with an extremely slow scan rate (often below 1 mVs^{-1}).^{42, 44, 49} In this section, the effect of dimensionless scan rate σ and the saturation parameter B on the resulting voltammograms will be investigated for two cases of g , first corresponding to no phase-transition behaviour and second for values of g beyond the critical value for a phase transition.

First, the effect of the dimensionless scan rate σ is studied for $g = -2.0$ (no phase transition) and $g = -5.0$ (phase transition). In the electro-sorption reaction, in the limit of an excess in the interfacial concentration of A compared to the number of surface sites the voltammetric response appears to be ‘surface-bound’ and the flux scales linearly with σ . Figure 7.8 shows the simulated voltammograms under reversible electrode kinetics ($K'_0 = 10^6$) with the y-axis normalised to σ . As can be seen, the voltammetric shape for $g = -2.0$ (no phase transition), under reversible electrode kinetics, are relatively unperturbed over three orders of magnitude of σ ; at a fast scan rate, $\sigma = 1000$, the voltammetric shape starts to flatten indicating a small degree of irreversibility. For a

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phase transition value of $g = -5.0$, however, the effect of σ is much more pronounced. The normalised peak flux J/σ is approximately three times larger with a decrease of σ from 1000 to 100, and from 100 to 10. This shows that voltammetry involving a phase transition is more sensitive to the value of σ compared to that with no phase transition behaviour. The physicochemical reasoning leading this observation in flux is discussed below in conjunction with results from varying the saturation parameter B .

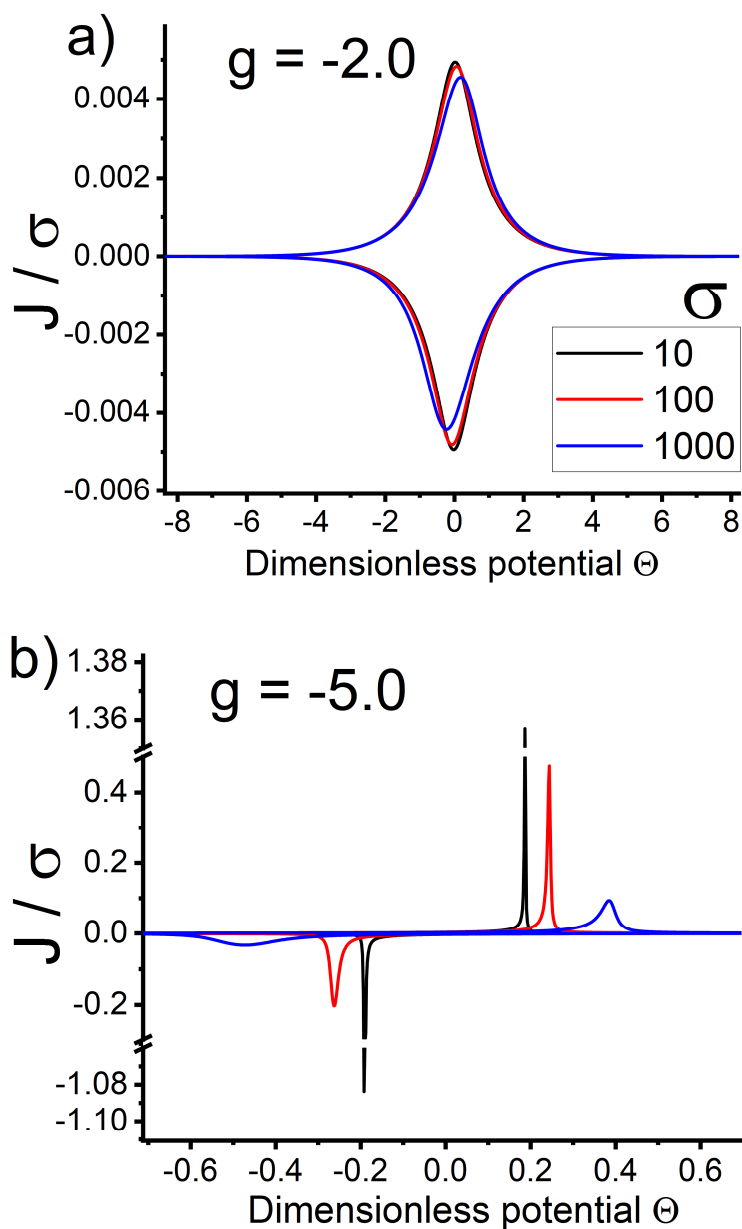


Figure 7.9. Simulated voltammograms as a function of dimensionless scan rate σ for two cases of non-ideal surface interaction a) $g = -2.0$ and b) $g = -5.0$. The values of σ and g are shown in the figure. Other simulation parameters: $K'_0 = 10^6$, $B = 100$, $\alpha = 0.5$ and $g^\ddagger = 0$.

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Next, the effects of the saturation parameter $B (\propto c_{A,bulk}/\Gamma_{max})$ under reversible electrode kinetics studied for $g = -2.0$ and $g = -5.0$ are shown in Figure 7.10 a) and b) respectively. For the electro-sorption voltammetry with no phase transition, Figure 7.10 a), varying B from 100 to 10,000 does not affect the voltammetric shape. The variation of saturation parameter B can be interpreted as the change in the experimental variable $c_{A,bulk}$ since Γ_{max} is usually constant. The voltammogram was not affected by the increase of B over two orders of magnitudes. This is because, already at the lowest saturation parameter studied ($B = 100$), under reversible electrode kinetics, the ‘surface-bound’ voltammetry as evident by the lack of diffusion tail precludes the depletion of $C_{A,0}$ throughout the voltammetric sweep. This, however contrasts with what is seen at a phase transition value of $g = -5.0$, shown in Figure 7.10 b). Here, an increase in B results in an increase in peak flux by a similar magnitude. The peak width, although it cannot be depicted easily, is reduced with the increase of B since the area under the peaks are necessarily the same.

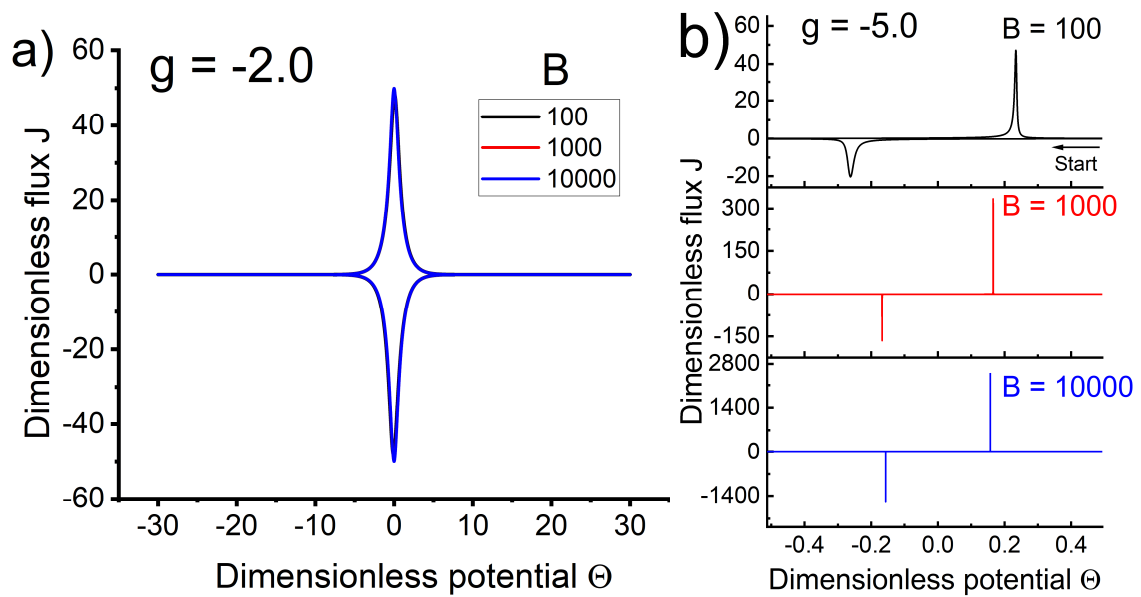


Figure 7.10. Simulated voltammograms as a function of B for two cases of non-ideal surface interaction a) non-phase transition $g = -2.0$ and b) phase transition $g = -5.0$. The values of g and B are shown in the figure. Other simulation parameters $K'_0 = 1E6$, $\sigma = 100$, $\alpha = 0.5$ and $g^\ddagger = 0$. The three lines coincide

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in a). The potential range for b) was reduced to $-5.0 \leq \theta \leq +5.0$ to improve temporal resolution; only part of the CV is displayed to improve visualisation.

To understand the effect of B has on the voltammetry with surface interactions leading to a phase transition, the simulation data in Figure 7.10 b) are shown in Figure 7.11 in a plot of θ_B against $\frac{KC_{A,0}}{K_{\theta_B=0.5}}$. The data for the forward sweep are plotted in Figure 7.11 a), and that of the backward sweep is plotted in Figure 7.11 b). The solid line is the corresponding analytical prediction from Frumkin adsorption isotherm. As can be seen, simulation data obtained for all values of B studied in Figure 7.10 b) are identical and with an excellent agreement to the adsorption isotherm. How then is this possible if the peak width and peak flux in the obtained voltammogram is different? It important to note that, the x- and y-axis in Figure 7.11, θ_B against $\frac{KC_{A,0}}{K_{\theta_B=0.5}}$ does not reflect the timescale of the forward deposition process. The dimensionless equilibrium constant K for the electro-sorption reaction is exponentially dependant on the dimensionless potential θ , and thus since the voltage is scanned also time dependant. However, the rate and magnitude of change in the interfacial $C_{A,0}$ during the voltammetry sweep is different for each value of B , shown in Figure 7.12. During the forward sweep ($0 \leq \frac{T}{T_{max}} < 0.5$), a drop in $C_{A,0}$ are seen around $\frac{T}{T_{max}} = 0.2$ and, on the reverse sweep, a sharp increase in $C_{A,0}$ are seen around $\frac{T}{T_{max}} = 0.8$. Inlay shows a zoom-in depicting the magnitude and the timescale of concentration change during the forward sweep. The minimum depletion of $C_{A,0}$ for $B = 100, 1000$ and 10000 is from 1.0 to 0.66, 0.72 and 0.73 respectively. Moreover, from the adsorption isotherm for $g = -5.0$, the recession of the ‘S-shaped’ transient occurs between x-axis values of 1.17 and 0.86. In the limiting case where the phase transition occurs instantaneously such that changes in K , with time, is assumed

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constant, the drop in $C_{A,0}$ during the forward sweep is has to be a minimum of 26% $\left(\frac{1.17-0.86}{1.17}\right)$. Thus, $C_{A,0}$ does not equate to $C_{A,bulk}$ at all times as the dynamic voltammetric waveforms necessary perturbs the interfacial concentration. The timescale at which phase transition occurs are reflected by the magnitude of the full width half maximum (FWHM) in the drop of $C_{A,0}$ with time, shown in the inlay of Figure 7.12. As can be seen, increasing B from 100 to 10000 leads to the phase transition timescale T/T_{max} from 10^{-3} to 10^{-7} .

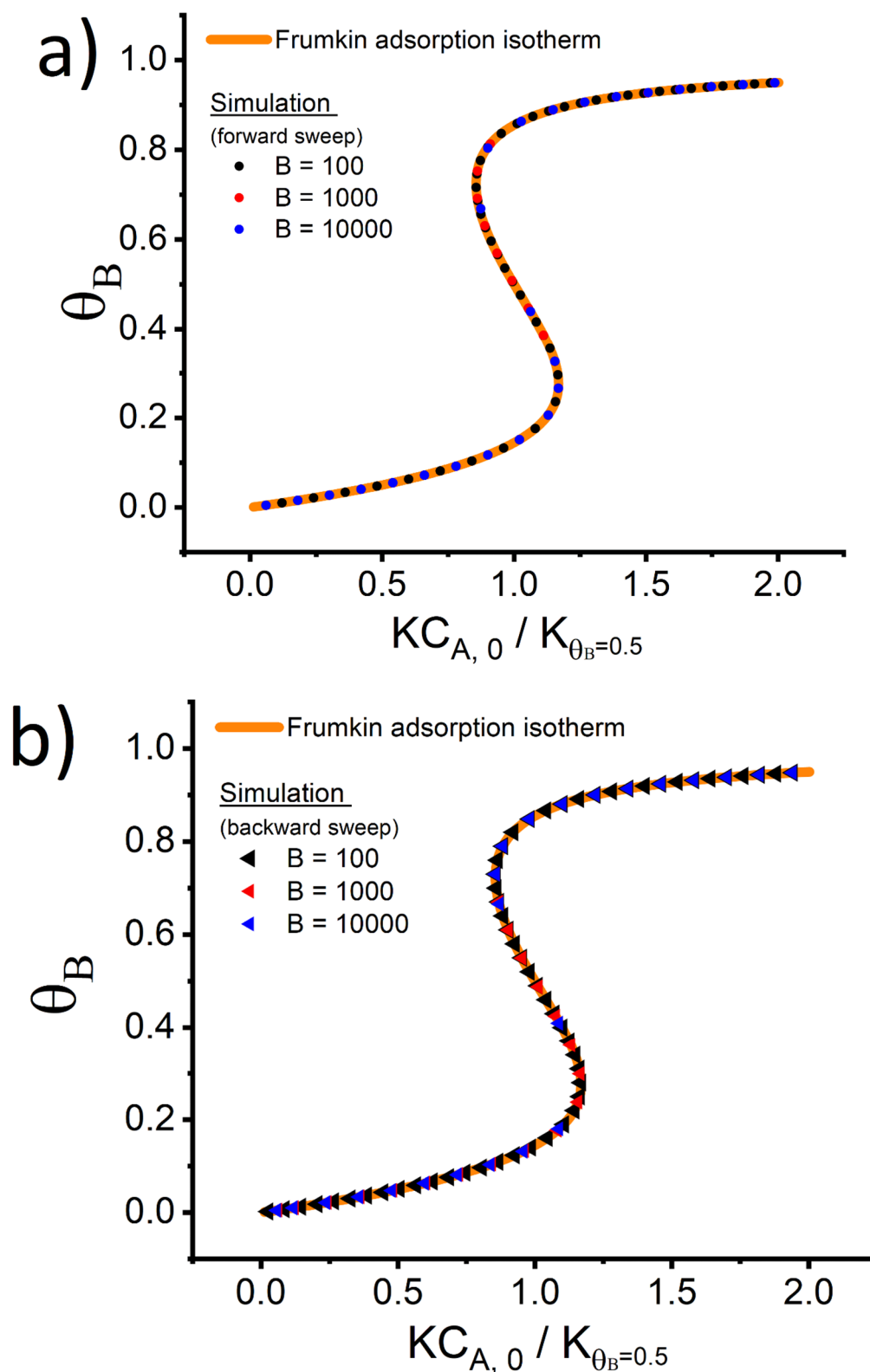


Figure 7.11. A plot of θ_B against $KC_{A,0}/K_{\theta_B=0.5}$ during the (a) forward and (b) voltammetry sweep for adsorbate-adsorbate interaction parameter $g = -5.0$. Solid line – Frumkin adsorption isotherm; Symbols (circle and triangles for forward and backward sweeps, respectively) – simulation data varying B from 100 to 10000 (CV shown in Figure 7.8 b). The values of B are shown in the figure. Other simulation parameters: $K'_0 = 1E6$, $\sigma = 100$, $\alpha = 0.5$, $g = -5.0$ and $g^\ddagger = 0$.

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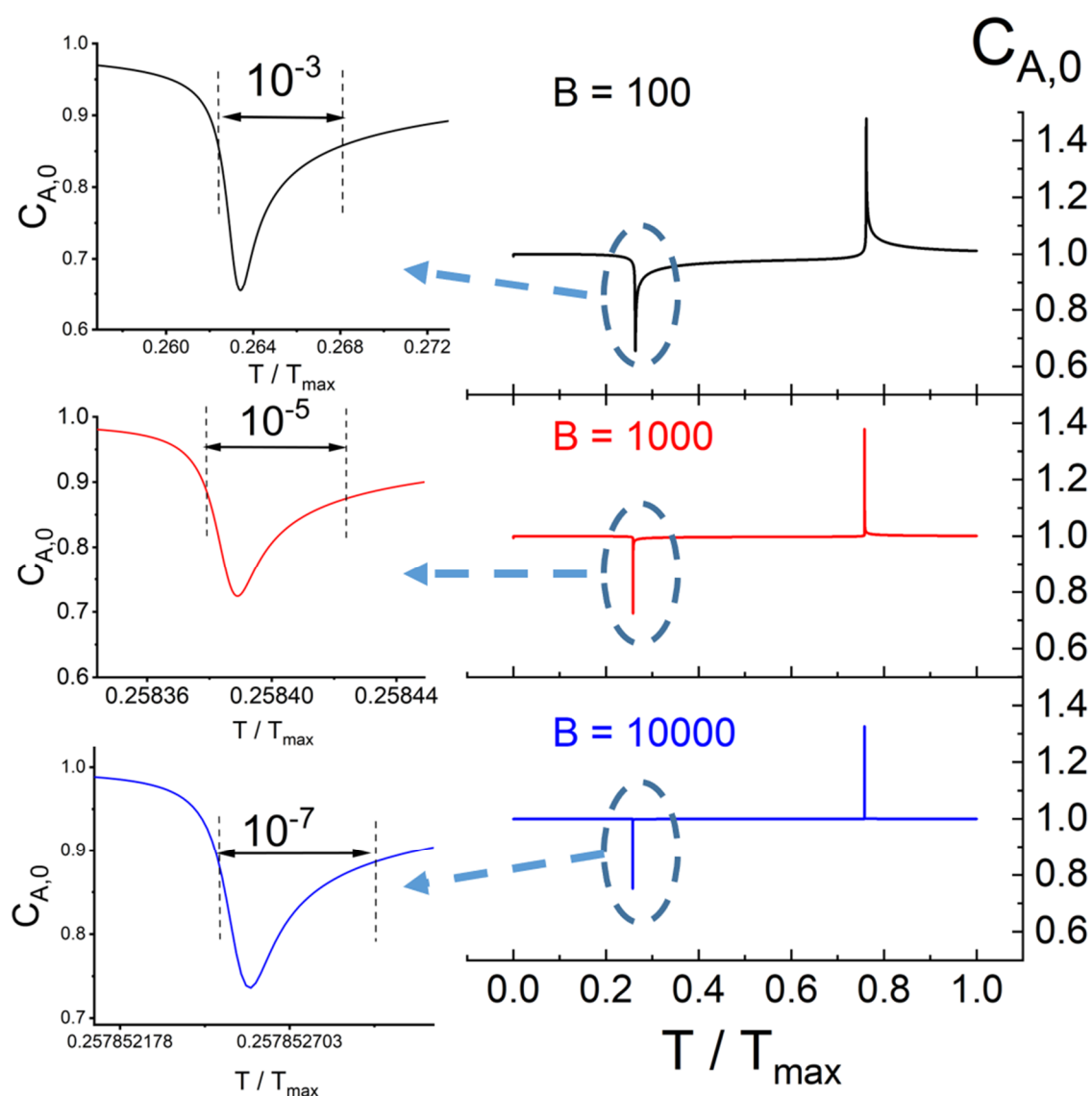


Figure 7.12. A plot of interfacial concentration $C_{A,0}$ for values of saturation parameter B ranging from 100 to 10,000 over the time scale of voltammetry with g equal to -5.0. The corresponding CV can be seen in Figure 7.10). The values of B are shown in the figure. Other simulation parameters: $K'_0 = 1E6$, $\sigma = 100$, $\alpha = 0.5$, $g = -5.0$ and $g^\ddagger = 0$. The inlay shows a zoom-in of the drop in $C_{A,0}$ during the forward sweep demonstrating the difference in the timescale.

7.4 Conclusions

This Chapter investigated a one-electron electro-sorption mechanism where the surface interactions are assumed non-ideal. The interfacial kinetics is described by Butler-Volmer kinetics coupled with Frumkin adsorption isotherm and with a bespoke formal potential, newly defined.

Herein, new physicochemical insights to phase transition behaviour under voltammetry conditions are provided from a simulation perspective. The novel use of a dimensionless equilibrium constant allowing the interfacial conditions during the voltammetry simulation to be compared with the Frumkin adsorption isotherm thus providing a new ground to understand the feasibility of voltammetric induced phase transitions. This directly leads to the observation that, fast and reversible electrode kinetics are essential in capturing the voltammetric induced phase transition leading to the sharp and narrow peaks, which otherwise, would lead to a ‘disconnection’ from the Frumkin adsorption isotherm.

Accounting for the non-equilibrium in mass transport when in analysing the voltammetry involving non-surface interactions is essential, particularly in the cases leading to phase transition. It is precisely this non-equilibrium in mass transport that causes the interfacial reaction to transit into the ‘forbidden zone’ of the Frumkin adsorption isotherm in voltammetry. Even if in the case of significant excess in bulk concentration the interfacial changes in concentration is non-negligible during a voltammetric induced phase transition; the simulation results show that, under reversible electrode kinetics, at least a 26% drop in the interfacial concentration $C_{A,0}$ is seen for $g = -5.0$. Thus, analysing voltammetric peak widths by assuming a diffusionless system, $C_{A,0} = C_{A,bulk}$ at all times, may lead to an underestimate of the value of g .

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Conclusions

The broad range work presented in this thesis, from experimental projects to theoretical simulations, illuminates upon the wealth of physicochemical processes within electrochemistry – it is full of challenges. To tackle some of the frontier electrochemical problems, my DPhil research devised bespoke electrochemical setups, combining in-situ electrochemical experiments with fluorescence microscopy or X-ray diffraction, and numerical simulations by writing C++ codes.

The generic and robust carbon/PVDF composite introduced in Chapter 2 allow *any* redox-active insoluble particles to be studied within the solvent potential window. Using this methodology, the cyclic voltammogram of α -HgS is reported for the first time. Moreover, when a mixture of sulphur and α -HgS are initially present in the composite, the re-oxidation peak potential of the sulphide ions was found to shift positively in the presence of a local mercury-rich environment, from -0.75V to -0.49V vs MSE. The mechanical rigidity of the carbon/PVDF composite and ease of modification allows the solid-state electrochemical experiment to be complementary studied simultaneously in situ with X-ray diffraction – revealing the electrochemical accessibility of the narrow phase width of β -Fe_{1+x}Se post-synthesis.

In Chapter 3, post-sonication electrochemical analysis of a mercury/water biphasic system reveals the concomitant formation of Hg@HgO core-shell particles *and* molecular Hg(OH)₂(aq). The former, Hg@HgO liquid core-shell particles is evidenced by X-ray diffraction and it provide an explanation to the grey, non-metallic appearance of the ‘emulsification’ and lack of coalescence with liquid mercury upon sedimentation. The latter, molecular Hg(OH)₂(aq), was electrochemically fingerprinted with a

Conclusions

concentration approaching the saturation limit of 0.24 mM after 60 minutes of insonation. These results are fully consistent with the ‘hot spot’ theory in sonochemistry, where cavitation results in the pyrolysis of water to form $\text{OH}\cdot$, which subsequently reacts with mercury. This study demonstrates the power of analytical electrochemistry and has the potential to detect mercury pollution in the environment existing in the form of $\text{Hg}(\text{OH})_2$. Chapter 4, *in situ* electrochemically generated radical species was found to irreversibly kill phytoplankton. The inhibition rate is evidenced to reflect neither the size nor the shape of the phytoplankton but most likely relates to the physical and chemical properties of the shell and outer membrane of the phytoplankton; the rate-determining step is the chemical destruction of the outer cellular structure. On a pragmatic level, the ability to differentiate between phytoplankton on the basis of their oxidative susceptibility has potential application in high-throughput methods for phytoplankton identification and bloom monitoring.

The simulation work in Chapter 6 investigates the effects of adsorption pathways on the voltammetric behaviour of surface-bound redox systems. The simulation work focuses on three different fates of the adsorbed product. Most noticeably, a steady-state current was seen on a macro-electrode reaches when the rate-determining step becomes ‘bottlenecked’ by the slow desorption of the product. Furthermore, when the rate of adsorption and desorption of the reaction and product are fast and not rate-determining, the simulated current for the redox process via the adsorption pathway can be ca. 2.3 times higher to that when electron transfer occurs via the solution phase. The distinctively different voltammetric features for each of the cases studied can be used to identify different adsorption pathways from experiments.

Continue from the simulation work of Chapter 6, Chapter 7 investigates the effect of surface interactions for a specific electro-sorption reaction. A voltammetric induced

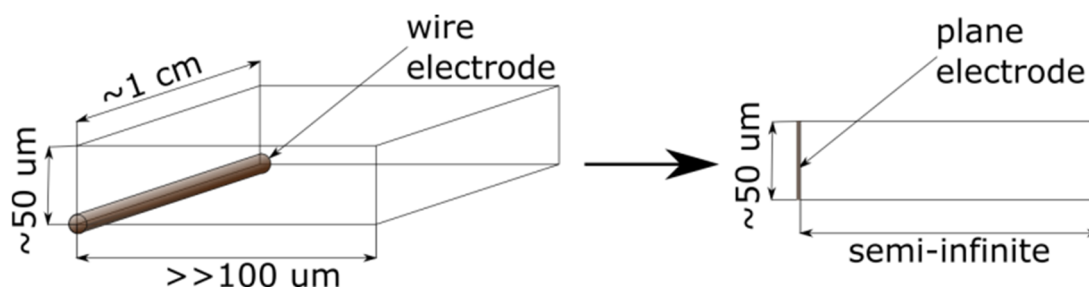
Conclusions

phase transition was predicted when the adsorbate-adsorbate interactions are strongly attractive; in which, fast and reversible electrode kinetics was necessary to capture such behaviour which results in sharp and narrow voltammetric peaks. If not otherwise, ‘disconnection’ from the Frumkin adsorption isotherm is seen. Moreover, the effect of mass transport non-equilibrium causes the interfacial reaction to transit into the ‘forbidden zone’ of the Frumkin adsorption isotherm in voltammetry. Even if in the case of significant excess in bulk concentration, the interfacial changes in concentration is non-negligible during a voltammetric induced phase transition. In light of the insights from simulation, analysing sharp UPD peak by assuming a diffusionless system, as is commonly the case in the literature, could lead to an underestimate of the value of g .

Appendix: A

Analytical Model for the Phytoplankton Fluorescence Response

In this section, we provide a simplified model of the phytoplankton response towards the production of radicals at the electrochemical interface. Specifically, we wish to provide insight into the physical factors controlling the ‘switching-off’ of the plankton fluorescence as a function of time and of distance to the electrode surface (as quantified in Figure 4.6 in the main text). Due to the necessary requirement of the reactive species diffusing away from the electrode surface before they can react with and induce damage to the phytoplankton, the resulting measured fluorescence response arises from a convolution of multiple physical and chemical factors.



Appendix A.1 Geometry of the actual cell and that used in the presented diffusional model. The electrochemical microscope cell contains a carbon fibre working electrode (radius $3.5 \mu\text{m}$, length $\sim 1 \text{ cm}$), in a thin-layer cell of $50 \mu\text{m}$ in height and with a width of far greater than $100 \mu\text{m}$. Note in the present work only the fluorescence response of plankton within approximately $100 \mu\text{m}$ of the wire electrode are monitored and analysed. In order to simplify the analysis the cell geometry is simplified to that of a one-dimensional problem.

Here, to provide a readily approachable model for this problem, it is assumed that the solution phase radical concentration must reach a threshold (C_{thres}) value, possibly required for the initial destruction of the cell wall, prior to inducing the oxidative destruction of the phytoplankton fluorescence response. Moreover, as depicted in Figure 4.2 the geometry of the cell can be simplified to become a one-dimensional problem.

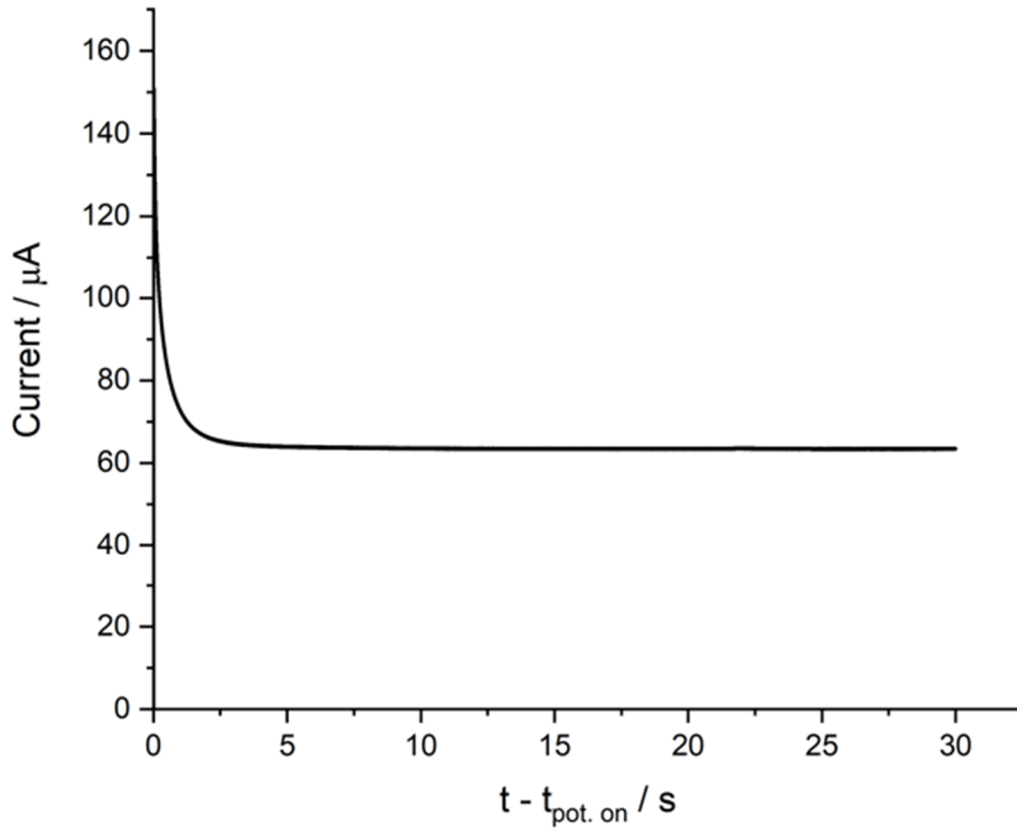
Appendix: A

In one dimension and in accordance with the Cottrell equation, the electrochemical flux (j /mol m⁻² s⁻¹) at the electrode interface can be described by:

$$j_{elec} = C_0 \left(\frac{D}{\pi t} \right)^{0.5} \quad (Eq. A.1)$$

where C_0 is the concentration at the electrode interface, D is the diffusion coefficient of the electroactive species (m² s⁻¹) and t is the experimental time (s). Given that in the experiment the solvent (water) is the electro-active reagent and that only a small fraction of the interfacial water is oxidised then, during the course of the chronoamperogram, the electrochemical (j_{elec}) flux will be relatively constant as a function of time. At +2.3 V vs Ag the recorded total current at the electrode was found to be ~60 μ A; an example experimental chronoamperogram is depicted in Appendix A.2 showing the steady-state nature of the current. In this section and as depicted in Appendix A.1, this model assumes that this current is produced at an electrode of dimensions 0.01 x 50 x 10⁻⁶ m². Hence, this gives an average electrochemical flux of approximately 1 x 10⁻³ mol m⁻² s⁻¹.

Appendix: A



Appendix A.2. Current-time transient during a typical fluoro-electrochemical chronoamperometry experiment. At $t - t_{\text{pot. on}} = 0$, the potential is stepped to $+2.3V$ vs Ag. where $t_{\text{pot. on}}$ is the time at which electrode potential is stepped to $+2.3V$.

In the timeframe of the experiment, the biologically dominant chemical species are the oxidative radicals produced by the electrochemical reaction. It is likely that only a small fraction of the current will lead to the production of radical species, such that the flux of radicals (j_{rad}) will be less than the electrochemical flux (j_{elec}). This may be expressed in a simple manner through accounting for the Faradaic efficiency (E_{ff}) of the interfacial reaction ($j_{\text{rad}} = E_{\text{ff}} j_{\text{elec}}$). In the following we assume an arbitrary efficiency of 1%. Hence, the interfacial radical flux (j_{rad}) is taken as a constant and given a value of $1 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1}$. Using and on the above argument setting the interfacial radical flux as a constant, the concentration of radicals ($C_{\text{rad}, x=0}$) at the interface can be approximately expressed as:

$$C_{\text{rad}, x=0} = j_{\text{rad}} \left(\frac{\pi t}{D} \right)^{0.5} \quad (\text{Eq. A. 2})$$

Appendix: A

This equation defines that under these constant electrochemical flux conditions the surface concentration of the radicals will approximately increase with the square-root of time.

In one dimension the concentration profile ($C(x, t)$) away from the electrochemical interface is:

$$C_{rad}(x, t) = C_{rad, x=0} \operatorname{erfc} \left(\frac{x}{2\sqrt{Dt}} \right) \quad (\text{Eq. A. 3})$$

where erfc is the complementary error function. Consequently, substitution of (Eq. A. 2 into Eq. A. 3, and setting $C(x, t)$ equal to some threshold concentration value gives the following:

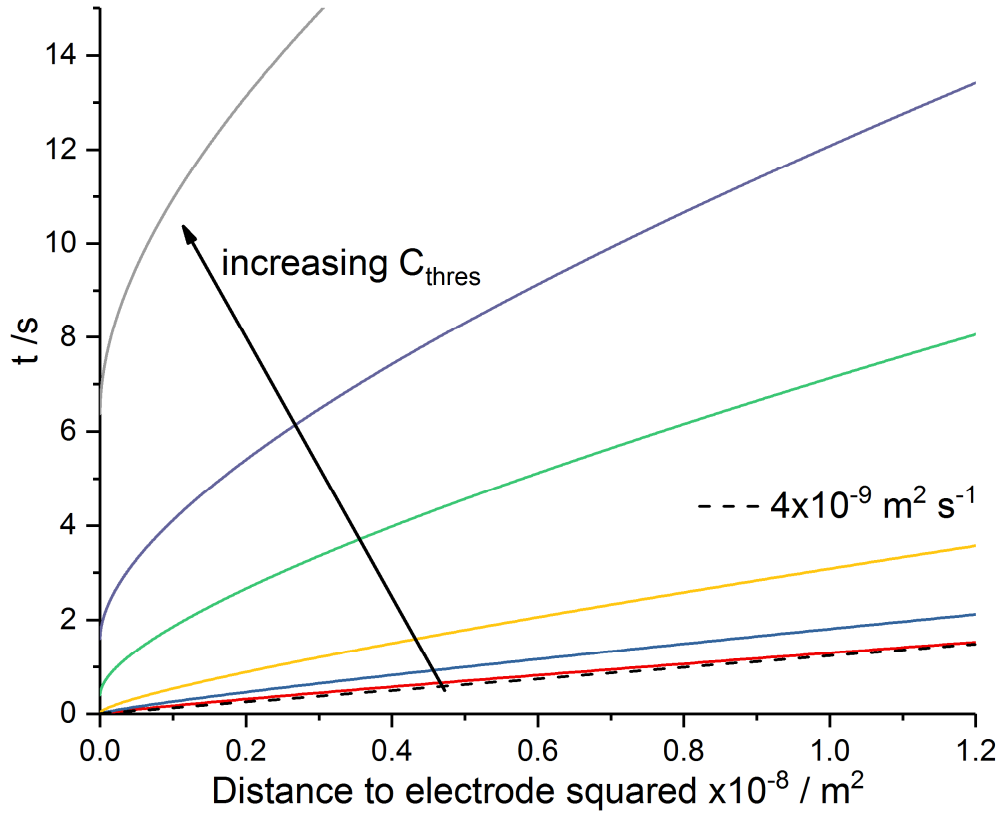
$$x = 2\sqrt{Dt} \operatorname{erfc}^{-1} \left(\frac{C_{thres}}{j_{rad}} \left(\frac{D}{\pi t} \right)^{0.5} \right) \quad (\text{Eq. A. 4})$$

where erfc^{-1} is the inverse complementary error function; the function here only yields physically relevant values when the input lies between 0 and 1, (Eq. A. 4 is an approximate analytical expression that describes how the distance at which the plankton fluorescence ‘switches-off’ varies as a function of: the experimental time, the radical diffusion coefficient, the flux of radical production at the electrode surface and the sensitivity of the plankton towards the radicals (as expressed through the value of C_{thres}).

To facilitate direct comparison of the above (Eq. A. 4 to the experimental results of different phytoplankton species as presented in Figure 4.13 a), Chapter 4. Appendix A. 3 plots the results of (Eq. A. 4 with differ values of C_{thres} (5×10^{-4} to 0.2 mM) as the distance squared against the time. Here we have taken a representative diffusion coefficient of $5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for the aqueous based species and have used the likely physically realistic radical flux (j_{rad}) of $1 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1}$. Also plotted is a reference

Appendix: A

line (dashed) of the equation $\langle x \rangle^2 = 2Dt$ where D has been given a value of $4 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, which is to be contrasted with the analytical result as discussed (varying C_{thres} with $D = 5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$).



Appendix A. 3. The predicted plankton fluorescence 'switch-off' time as a function of the distance from the electrode surface, as given by the approximate analytical (Eq. A. 4. $D_{\text{rad}} = 5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $j_{\text{rad}} = 1 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1}$, $C_{\text{thres}} = 5 \times 10^{-4} \text{ mM}$ (red), 0.002 mM (blue), 0.01 mM (yellow), 0.05 mM (green), 0.1 mM (purple) and 0.2 mM (grey). Also overlaid for comparison with a dashed line is the expression $t = x^2 / 2D_{\text{eff}}$, where here effective diffusion coefficient (D_{eff}) has been given a value of $4 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$.

Appendix A. 3 presents a number of important features. First, the value of C_{thres} partially controls the time at which the phytoplankton fluorescence responds to the electro-generated oxidative species; for a given electrode radical flux higher values of C_{thres} increases the time required – at a given distance from the electrode – for the fluorescence to be affected. Second, a non-zero intercept is predicted at high threshold values. Third, in the long time limit or for low threshold values the plot becomes quasi-linear. This quasi-linearity arises for small values of the input of the erfc^{-1} function. Although erfc^{-1}

Appendix: A

tends to infinity at zero it does so very slowly, consequently for reasonable values of the input value to the erfc^{-1} function it has an approximate limit of ~ 2 . Consequently, in this low C_{thres} or long time limit (Eq. A. 4 becomes approximately equal to $x = 4\sqrt{Dt}$ ($t = x^2/16D$), where in this analysis the value of D has been taken as $5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. Hence, for the C_{thres} value of $5 \times 10^{-4} \text{ mM}$, as plotted in Appendix A. 3, (Eq. A. 4 is approximately equal to the equation $t = x^2/2D_{\text{eff}}$, where the effective diffusion coefficient has a value of $4 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$, this is plotted as the dashed line on Appendix A. 3. Fourth, As the concentration threshold is increased the output of the erfc^{-1} function decreases leading to a change in the gradient of the plot, the curvature present for the high c_{thres} values (0.2 mM for example) reflects, in this limit, the variability of the erfc^{-1} function with time.

In Chapter 4, the gradient of the plot of the fluorescence ‘switch-off’ time against the distance the phytoplankton is away from is used as a measure of the microalgal sensitivity towards oxidative radical damage. The gradient is reported as a *susceptibility factor*, as related to the inverse gradient of a plot of time vs distance squared. This analysis shows that this “effective” diffusion coefficient represents the mass-transport of the radical species multiplied by some unknown but species specific ‘phytoplankton’ sensitivity factor towards the generated radical. As demonstrated above this effective diffusion coefficient can be larger than the actual diffusion coefficient of the molecular (radical) species. The measured effective diffusion coefficient will also be sensitive to the magnitude of the experimentally used oxidative flux (j_{rad}). High values of the measured susceptibility factor indicate a relative high sensitivity or vulnerability of the plankton towards oxidative radical attack; conversely, lower values indicate increased plankton resilience. Given in this work the chemical conditions are the same throughout the work such that the radical diffusion coefficient and electrode flux are essentially constants then

Appendix: A

the measured susceptibility factor for the different phytoplankton can be used a direct comparator of the different species sensitivity towards oxidative radical attack.

Appendix: B

Appendix: B presents the derivation and plots which together benchmark the simulation model discussed in Chapter 7 – “Voltammetry of Adsorbed Species: Non-ideal Interactions Leading to Phase Transitions”.

Limiting Case One

For a simple one-electron transfer reaction with irreversible electrode kinetics, the peak current of the forward voltage sweep is described by the irreversible Randles–Ševčík equation^{1,2}

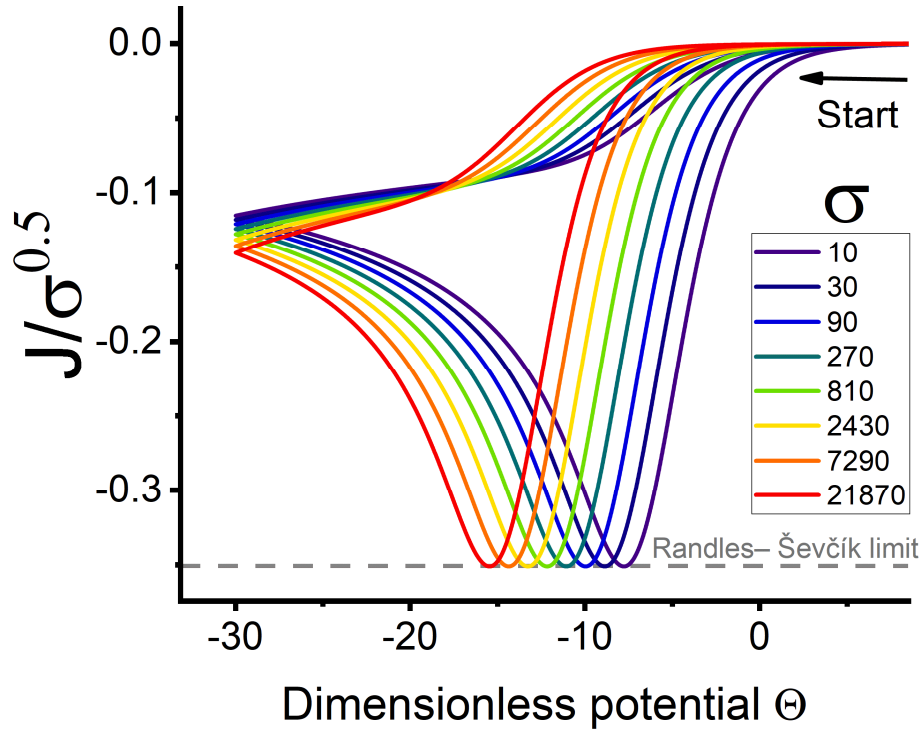
$$I_{peak, irreversible Randles-Ševčík} = 2.99 \times 10^5 \alpha^{1/2} A C_{A,bulk} D^{1/2} v^{1/2} \quad (Eq. B.1)$$

This can be expressed in dimensionless form using the definitions given in Table 7.1

$$J_{peak, irreversible Randles-Ševčík} = -0.496 \sqrt{\alpha \sigma} \quad (Eq. B.2)$$

In the limiting case for the one-step electro-sorption reaction, $A(aq) + e^- + M(site) \rightleftharpoons B(ads)$, small adsorption-desorption rate constants *and* sufficiently large surface coverage, such that less than ca 1% of the sites are occupied, the resulting peak flux shown in Appendix B.1 matches with that predicted by the irreversible Randles–Ševčík Equation B.2 with excellent agreement.

Appendix: B



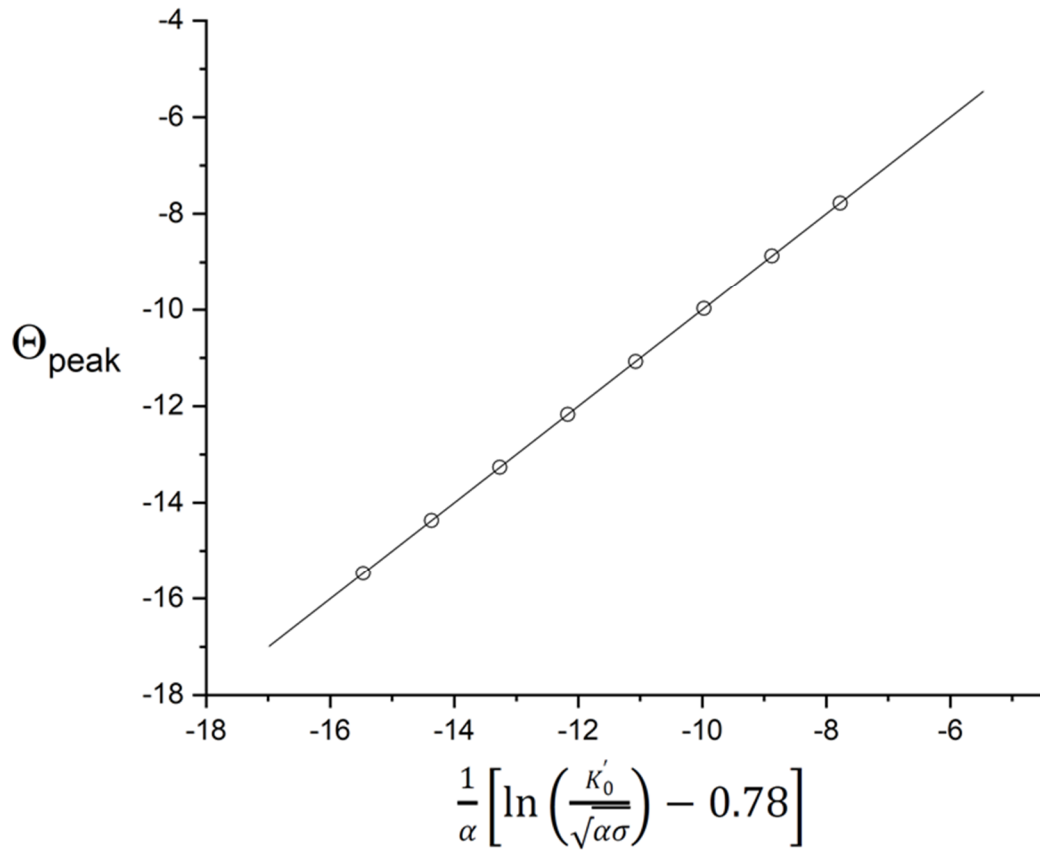
Appendix B.1. Simulated voltammograms for limiting Case One at different σ . Other simulation parameters: $K'_0 = 0.1$, $B = 0.0001$, $\alpha = 0.5$, $g = 0$ and $g^\ddagger = 0$. Note that no more than 1% of the total sites are occupied at any given time during the simulation.

Furthermore, an expression for the dimensionless peak potential Θ_{peak} in the limit of irreversible kinetics is known and can be adapted for this limiting case³

$$\Theta_{peak, \text{ limiting Case One}} = \frac{1}{\alpha} \left[\ln \left(\frac{K'_0}{\sqrt{\alpha\sigma}} \right) - 0.78 \right] \quad (\text{Eq. B.3})$$

Equation B.3 is shown as a line plot in Appendix B.2 with data obtained from the simulated voltammograms as seen in Appendix B.1 overlaid as circles. Excellent agreement is seen.

Appendix: B



Appendix B.2. A plot of the analytical expression of peak potential, Equation B.3 (solid line), against data obtained from simulated voltammograms in Appendix B.1.

Limiting Case Two

This sub-section benchmarks the backward electro-desorption step with analytical expressions obtained for irreversible electrode kinetics. First, a step-by-step derivation for the expressions of peak flux and peak potential for this limiting case is developed below. This is followed by a comparison of the underlying theory with the simulation results, showing excellent agreement for both peak flux and peak potential for the case where the surface has a full initial coverage of θ_B .

Boundary Conditions and Analytical expressions

At $T = 0$, the initial fractional coverage θ_B is set to unity with a varying anodic applied potential θ driving the oxidation of $B(ads) \rightarrow A(aq)$.

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$$\theta = \theta_{initial} + \sigma T \quad (Eq. B.4)$$

The value of the initially applied potential $\theta_{initial}$ is selected to ensure no oxidation reaction occurs at $T = 0$. The dimensionless flux J , as defined in the main text (Equation 7.35) now becomes

$$J_{limiting\ case\ 2} = -\frac{1}{B} \frac{\partial \theta_B}{\partial T} = K'_{ox} \theta_B e^{(g-g^\ddagger)\theta_B} \quad (Eq. B.5)$$

where the forward electro-deposition term, by assumption, contributes negligibly to the overall flux and thus can be neglected. Substituting the definition of K'_{ox} (Equation 7.36) into Equation B.5 gives

$$J_{limiting\ case\ 2} = K'_0 c^0 e^{g/2} e^{(1-\alpha)\theta} \theta_B e^{(g-g^\ddagger)\theta_B} \quad (Eq. B.6)$$

In the limiting case when $g = g^\ddagger = 0$ gives

$$J_{limiting\ case\ 2} = -\frac{1}{B} \frac{\partial \theta_B}{\partial T} = K'_0 e^{(1-\alpha)\theta} \theta_B \quad (Eq. B.7)$$

Since the dimensionless potential θ is a function of time T (Equation B.4), an expression of coverage θ_B with respect to T can be obtained via integration

$$\int_{T=0}^T \frac{1}{\theta_B} d\theta_B = -BK'_0 \int_{T=0}^T e^{(1-\alpha)(\theta_{initial} + \sigma T)} dT \quad (Eq. B.8)$$

$$[\ln \theta_B]_{T=0}^T = -\frac{BK'_0}{(1-\alpha)\sigma} [e^{(1-\alpha)(\theta_{initial} + \sigma T)}]_{T=0}^T \quad (Eq. B.9)$$

substituting the boundary condition ($T = 0, \theta_B = 1$) gives

$$\ln \theta_B (T) = -\frac{BK'_0}{(1-\alpha)\sigma} (e^{(1-\alpha)(\theta_{initial} + \sigma T)} - e^{(1-\alpha)\theta_{initial}}) \quad (Eq. B.10)$$

Equivalently, and more conveniently, this can be expressed as a function of the dimensionless applied potential θ

$$\ln(\theta_B(\theta)) = -\frac{BK'_0}{(1-\alpha)\sigma} * (e^{(1-\alpha)\theta} - e^{(1-\alpha)\theta_{initial}}) \quad (Eq. B.11)$$

Appendix: B

Since in this limiting case, the value of $\theta_{initial}$ is sufficient negative so no oxidation occurs at $T = 0$, and θ is always greater than $\theta_{initial}$; to a good approximation, Equation B.11 can be reduced to

$$\ln(\theta_B(\theta)) = -\frac{K'_0 B}{(1-\alpha)\sigma} e^{(1-\alpha)\theta} \quad (Eq. B.12)$$

Taking the natural logs on both sides of the equation

$$\theta_B(\theta) = e^{-\frac{K'_0 B}{(1-\alpha)\sigma} e^{(1-\alpha)\theta}} \quad (Eq. B.13)$$

Next, substituting Equation B.13 back to Equation B.7 gives an analytical expression for dimensionless flux J as a function of the dimensionless potential θ

$$J_{limiting\ case\ 2} = K'_0 e^{(1-\alpha)\theta} e^{-\frac{K'_0 B}{(1-\alpha)\sigma} e^{(1-\alpha)\theta}} \quad (Eq. B.14)$$

Furthermore, the peak dimensionless potential θ_{peak} can be found when the derivative of J with respect to θ equals zero

$$\begin{aligned} \frac{\partial J_{limiting\ case\ 2}}{\partial \theta} &= K'_0 \left((1-\alpha) e^{(1-\alpha)\theta_{peak}} e^{-\frac{K'_0 B}{(1-\alpha)\sigma} e^{(1-\alpha)\theta_{peak}}} - \frac{K'_0 B}{\sigma} e^{(1-\alpha)2\theta_{peak}} e^{-\frac{K'_0 B}{(1-\alpha)\sigma} e^{(1-\alpha)\theta_{peak}}} \right) \\ &= 0 \end{aligned} \quad (Eq. B.15)$$

The common terms in Equation B.15 can be simplified to

$$(1-\alpha) - \frac{K'_0 B}{\sigma} e^{(1-\alpha)\theta_{peak}} = 0 \quad (Eq. B.16)$$

Rearrangement gives the expression for θ_{peak}

$$\theta_{peak} = \frac{1}{1-\alpha} \ln \left(\frac{(1-\alpha)\sigma}{K'_0 B} \right) \quad (Eq. B.17)$$

Finally, substituting Equation B.17 into Equation B.14 gives an expression of peak flux of limiting Case Two, $J_{peak, limiting\ case\ 2}$

Appendix: B

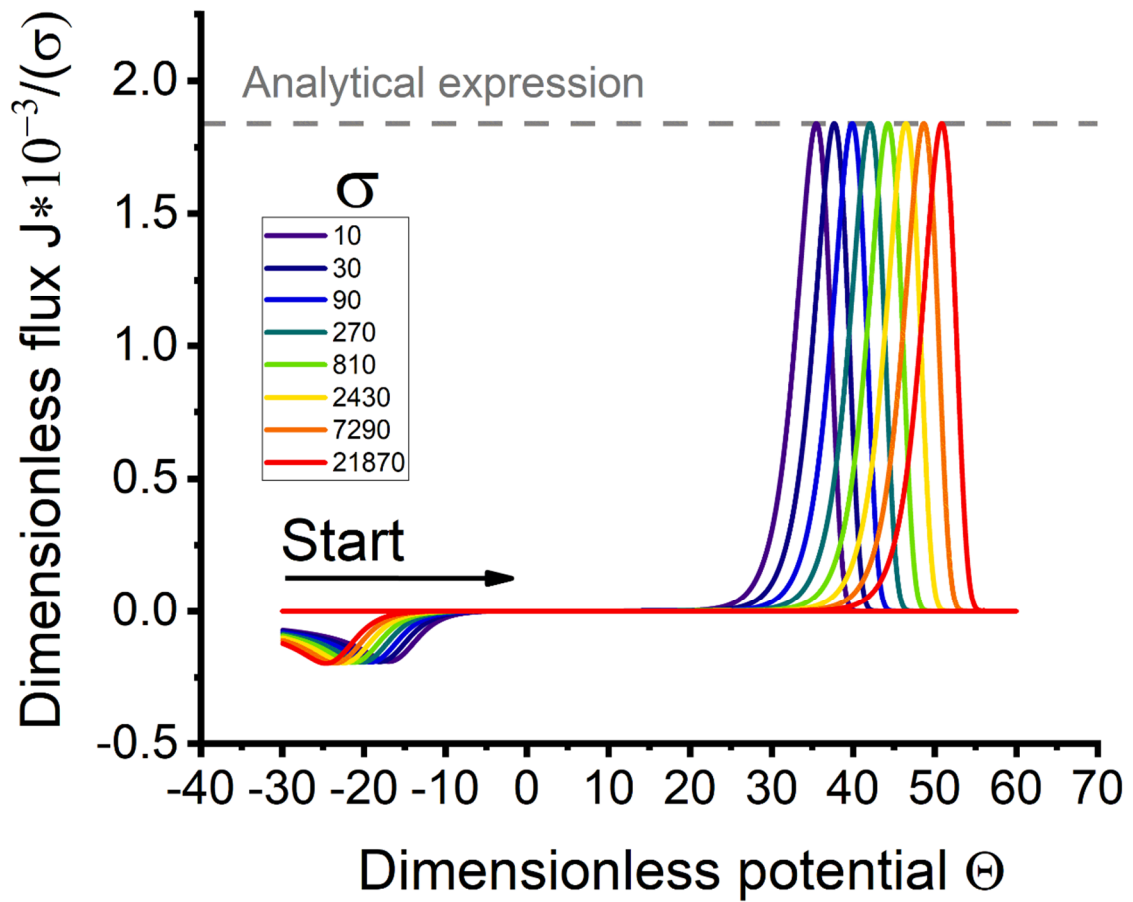
$$J_{peak, \text{ limiting case 2}} = K'_0 e^{(1-\alpha) \frac{1}{1-\alpha} \ln\left(\frac{(1-\alpha)\sigma}{K'_0 B}\right)} e^{-\frac{K'_0 B}{(1-\alpha)\sigma}} e^{(1-\alpha) \left(\frac{1}{1-\alpha} \ln\left(\frac{(1-\alpha)\sigma}{K'_0 B}\right)\right)} \quad (\text{Eq. B.18})$$

Simplifying gives

$$J_{peak, \text{ limiting case 2}} = (1 - \alpha) \sigma B^{-1} e^{-1} \quad (\text{Eq. B.19})$$

Simulation for limiting Case Two

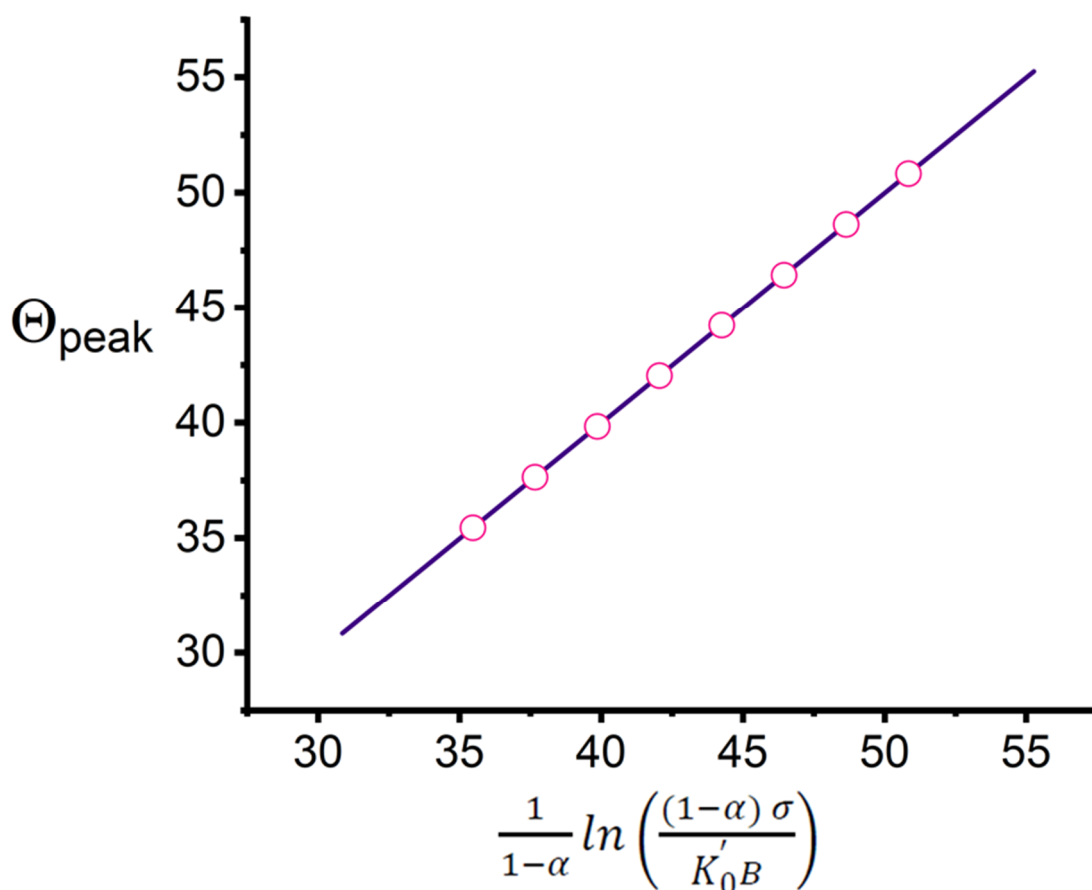
Appendix B.3 shows the simulated voltammograms for limiting Case Two at different dimensionless scan rates σ ; initially only a monolayer of B(ads) is present and the peak flux during the oxidative potential sweep matches the analytical expression derived above (Equation B.19).



Appendix B.3. Simulated voltammograms for limiting Case Two for different scan rate σ . Other simulation parameters: $K'_0 = 0.001$, $B = 10^{-4}$, $\alpha = 0.5$, $g = 0$ and $g^\ddagger = 0$. Overlaid as dotted line is the analytical expression for $J_{peak, \text{ limiting case 2}}$ as shown in Equation B.19.

Appendix: B

Furthermore, Appendix B.4 shows the analytical expression for peak potential from Equation B.17 as a solid line and overlaid as circles are the data from the simulated voltammograms plotted in Appendix B.3. Again, the agreement is excellent.



Appendix B.4. A plot of the analytical expression of peak potential for limiting Case Two, Equation B.17(solid line), against data obtained from simulated voltammograms in Appendix B.3.